



LIBRARY
OF THE
UNIVERSITY
OF ILLINOIS


546
I-l6i
1949/50



Return this book on or before the
Latest Date stamped below.

University of Illinois Library

L161—H41



Digitized by the Internet Archive
in 2012 with funding from
University of Illinois Urbana-Champaign

<http://archive.org/details/inorganicsemi194950univ>

TABLE OF CONTENTS

1949 - 1950

| | Page |
|--|------|
| ACETIC ANHYDRIDE AS A SOLVENT AND REACTION MEDIUM John R. Kuebler, Jr. | 1 |
| COMPLEXING ACTION OF ETHYLENEDIAMINETETRAACETIC ACID R. L. Dalton | 7 |
| RECENT DEVELOPMENTS IN THE CHEMISTRY OF META_ PYRO_ AND POLYPHOSPHATES Emil W. Grieshaber | 11 |
| ELECTROCHEMICAL PROPERTIES OF FUSED SALT SYSTEMS M. Krulfeld | 16 |
| SOME PHYSICAL AND CHEMICAL PROPERTIES OF SOLID SUBSTANCES AS A FUNCTION OF SIZE - CHARGE RELATIONSHIPS Andrew J. Frank | 23 |
| COORDINATION OF RARE GASES WITH BORON TRIFLUORIDE G. L. Eichhorn | 31 |
| SELECTIVE CATALYSIS F. R. Pundsack | 31 |
| THE AWUEOUS CHEMISTRY OF ZIRCONIUM Allan D. Gott | 32 |
| THE CHROMATOGRAPHIC SEPARATION OF PERRHENIC AND MOLYBDIC ACIDS J. N. Coker | 33 |
| EXAMPLES OF ACID-BASE RELATIONSHIPS IN NON-AQUEOUS SYSTEMS Wm. A. Ziegler | 34 |
| HIGHER OXIDES OF THE ACTINIDE ELEMENTS. THE PREPARATION OF Np_2O_5 (1) Therold Moeller | 35 |
| THE ACIDS OF THE HYDROGEN FLUORIDE SYSTEM Montfort A. Johnsen | 37 |
| THE NOMENCLATURE OF ORGANOSILICON COMPOUNDS Thomas G. Miller | 44 |
| URANIUM HYDRIDE Gladys H. Quinty | 51 |
| LIQUID DINITROGEN TETROXIDE SOLVENT SYSTEM Ralph Gher | 57 |
| ISOTOPIC EXCHANGE BY ELECTRON TRANSFER BETWEEN COMPLEX IONS John E. McNamara | 63 |
| SODIUM-TUNGSTEN BRONZES J. A. Fuller | 70 |

| | |
|--|-----|
| OXIDATION AND REDUCTION IN GEOCHEMISTRY Pranlal G. Sheth | 74 |
| STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS Leo F. Meneghan | 78 |
| A POLAROGRAPHIC STUDY OF SOME INORGANIC COMPLEXIONS E. I. Onstott | 79 |
| THE PHOSPHATES AND POLYPHOSPHATES OF THE RARE EARTHS AND THORIUM A. G. Buyers | 81 |
| INORGANIC COMPLEX COMPOUNDS CONTAINING POLYDENTATE GROUPS Allan D. Gott | 85 |
| CHEMISORPTIVE BONDS AND CATALYSIS S. M. Cohen | 87 |
| SYNTHESIS GASES Homer J. Birch | 90 |
| THE PEROXY COMPLEXES OF PLUTONIUM (IV) Richard L. Dalton | 92 |
| REACTIONS OF BROMINE TRIFLUORIDE L. F. Audrieth | 94 |
| THE DISSOLUTION OF ALUMINUM IN SODIUM HYDROXIDE SOLUTIONS Donald P. Hallada | 96 |
| THE STRUCTURE OF PENTACOVALENT COMPOUNDS Arthur M. Ross | 98 |
| BOND LENGTHS IN SOME INORGANIC MOLECULES George Speranze | 101 |
| ORGANOGERMANIUM COMPOUNDS Robert F. Vance | 103 |
| CRYSTAL GROWTH - I. GENERAL THEORY Alan L. McClelland | 105 |
| CRYSTAL GROWTH - II. LAYER FORMATION ON CRYSTAL FACES Dale E. Jackson | 106 |
| CRYSTAL GROWTH - III. HIGH TEMPERATURE CRYSTAL GROWTH Paul H. Mohr | 107 |
| CRYSTAL GROWTH - IV. CRYSTAL HABIT MODIFICATION AS A MEANS OF REDUCING CAKING OF SALTS R. Keith Osterheld | 108 |
| CRYSTAL GROWTH - V. THE EFFECTS OF RADIATIONS ON CRYSTALS W. B. Schaap | 109 |

| | Page |
|---|------|
| METALLIC COMPLEXES OF BIGUANIDE AND ITS DERIVATIVES J. R. Kuebler, Jr. | 110 |
| DISPROPORTIONATION IN INORGANIC COMPOUNDS Gladys H. Quinty | 113 |
| TITRIMETRY IN NON-AQUEOUS SOLUTIONS William A. Ziegler | 115 |
| HYDROGEN POLYSULFIDES S. H. Pines | 119 |
| THE DESIGNATION OF SPECIAL ISOTOPES IN THE NAMES AND FORMULAS OF INORGANIC COMPOUNDS L. Elmer Olson | 122 |
| STABILIZATION OF UNUSUAL OXIDATION STATES BY FORMATION OF PERIODATES AND TELLURATES Melvin Tecotzky | 125 |
| CATALYTIC ACTIVITY OF METALS PRODUCED BY REDUCTION IN LIQUID AMMONIA William W. Campbell | 127 |
| FLUORIDES OF CARBON Montfort A. Johnsen | 129 |
| FORMATION AND STABILITY OF BINARY INORGANIC COMPOUNDS William W. West | 132 |
| CUPROUS CHLORIDE COMPLEXES OF MALEIC AND FUMARIC ACIDS David Carley | 134 |
| COMPLEXES BETWEEN METAL SALTS AND LONG-CHAIN ALIPHATIC AMINES Sheldon S. Simon | 137 |
| PHASE EQUILIBRIUM OF THE SYSTEM SULFUR TRIOXIDE AND WATER L. F. Audrieth | 139 |
| ELECTROCHEMICAL STUDIES OF SOME COORDINATION COMPOUNDS OF IRON Ward B. Schaap | 140 |
| AUTOXIDATION OF HYDRAZINE Paul H. Mohr | 142 |
| 8-QUINOLINOL AND SUBSTITUTED 8-QUINOLINOL CHELATES OF CERTAIN RARE EARTH ELEMENTS Dale E. Jackson | 145 |
| ELECTROCHEMICAL STUDIES OF SOME COORDINATION COMPOUNDS OF SILVER Alan L. McClelland | 148 |
| POLY- AND METAPHOSPHATES R. Keith Osterheld | 150 |

ACETIC ANHYDRIDE AS A SOLVENT AND REACTION MEDIUM

John R. Kuebler, Jr.

October 4, 1949

INTRODUCTION

Three major acid-base theories are at the present time in general use (1). The broadest of these is the Lewis theory, defining acids as molecules capable of accepting an electron pair, bases as molecules capable of donating an electron pair, and does not necessarily limit acid-base reactions to a solvent. On the other hand, the Bronsted concept is the most limited, as it restricts acids and bases to substances that can donate or accept protons, respectively. Intermediate between these two extremes is the solvent system theory. The early work dealt chiefly with solvents containing a replaceable proton, such as liquid NH_3 and anhydrous acetic acid. This concept was later extended to include non-protonic, non-aqueous solvents like liquid SO_2 . Gady and Elsey (2) defined an acid as any solute giving a cation characteristic of the solvent, and a base as any solute giving an anion characteristic of the solvent. Although this theory emphasizes that acid-base behavior is not confined to solutions containing proton donors, it does have the disadvantage of limiting acid-base reactions to a given solvent system and (from the point of view of the Lewis theory) places undue importance on ionization as the most important factor in acid-base properties. Jander has adopted the definitions of Gady and Elsey; consequently, these will be used exclusively in a discussion of acetic anhydride as a solvent and reaction medium.

ACETIC ANHYDRIDE AS A SOLVENT

Jander and co-workers have recently investigated the solvent and reaction characteristics of acetic anhydride (3,4,5). That this material possesses the characteristics of a typical non-protonic solvent is evident from a comparison of its physical properties with those of water, on the one hand, and two non-protonic solvents, I_2 and SO_2 .

TABLE I

| Solvent | Mole Wt. | M.P. | B.P. | Dielect. Const. | Conductivity (Recip. ohm) | Viscosity η (dyne-sec/cm) |
|--------------------|----------|------|------|-----------------|--|--------------------------------|
| Acetic Anhydride | 103 | -73° | 140° | 20.5 | 2×10^{-7} to 5×10^{-7} | 0.0085 |
| Water | 18 | 0° | 100° | 81 | 4.4×10^{-7} | 0.0030 |
| Iodine | 254 | 113° | 183° | 11-13 | 1×10^{-4} | 0.0141 |
| Liq. SO_2 | 64 | -76° | -10° | 13.8 | 1×10^{-7} | 0.0039 |

Jander (6) has also listed the characteristic chemical and physical properties of non-aqueous solvents, of which the following are exhibited by acetic anhydride:

- 1) It dissolves many inorganic and organic substances (3).
- 2) The pure solvent is a poor conductor (3,4), while many



solutions are comparatively highly conducting (7) with electrolytic decomposition going on at the electrodes (5).

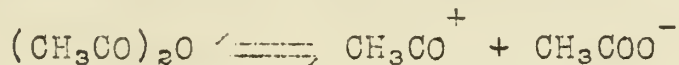
3) It has long been known that some metal acetates form stable solvates of the type $(\text{CH}_3\text{COOMe})_2 \cdot (\text{CH}_3\text{CO})_2\text{O}$ (8,9).

4) Acid and base analogs undergo neutralization reactions to form salts and the solvent. As a rule acetyl compounds are weak acid analogs, while acetates are strong base analogs.

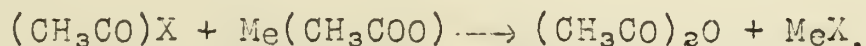
5) Many metal salts and acidic halides undergo solvolytic reactions to form acid and base analogs (4).

NEUTRALIZATION REACTIONS IN ACETIC ANHYDRIDE (3)

Analogous to other non-aqueous solvents, the low conductivity of pure acetic anhydride is assumed to be due to a limited auto-ionization in accordance with the equilibrium:



Solutions of acetyl compounds and acetates were shown to undergo neutralization reactions of the type:



The acetic anhydride was prepared by the method of Walton and Withrow (10) to effect removal of the acetic acid impurity. Neutralization reactions were followed conductometrically.

Three types of conductometric curves were obtained, depending upon whether the salt formed was found to be insoluble, partly soluble, or completely soluble in acetic anhydride (Fig. 1).

Curve I illustrates the case where the salt formed is almost insoluble in acetic anhydride. (NaCl , KCl , TlCl , TlBr , TlSCN , Ag_2S , PbS .)

Curve II represents the case of a slightly soluble salt (RbCl , RbBr , CsBr). The conductivity initially increases as long as the salt is soluble, but when the limit of solubility is reached, there is a break in the curve, and the conductivity decreases until the equivalence point is reached, after which it remains essentially constant.

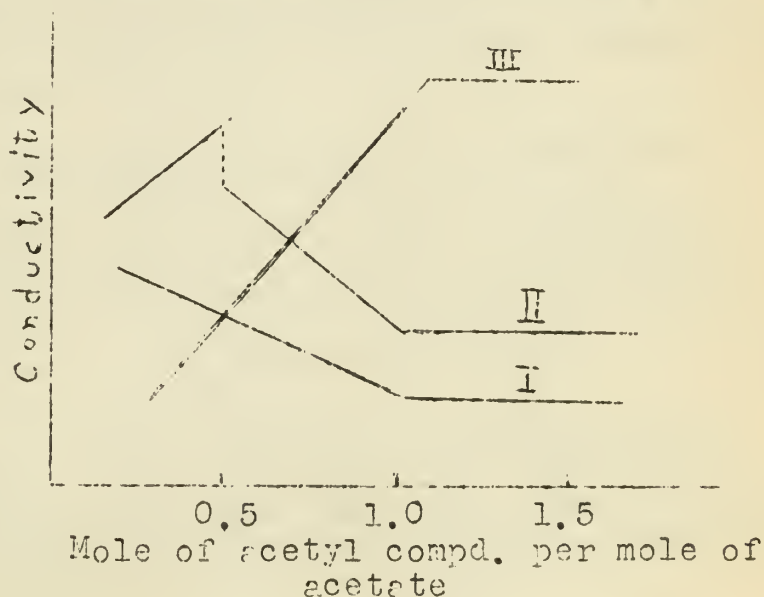
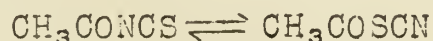


Fig. 1

Curve III is typical of those cases which involve formation of a soluble salt. Reactions proceeded as expected except in the following three cases:

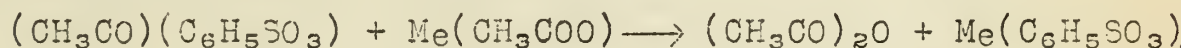
Thiocyanate Salts: The thiocyanate salts formed initially react with the solvent, possibly to form triacetyl nitride, which is itself unstable and decomposes further. The long period required for the stabilization of the conductivity values after each addition of the acetyl thiocyanate was explained on the basis of previous work by Hawthorne (11), who concluded from a study of molar refraction values that acetyl thiocyanate (CH_3COSCN) actually consists largely of acetyl isothiocyanate (CH_3CONCS) in equilibrium with some of the thiocyanate. Consequently, the slow stabilization of the conductivity was attributed to the time involved in forcing the equilibrium



to the right as the thiocyanate was used in the reaction.

Acetyl Sulfide: Alkali sulfides are solvolyzed by acetic anhydride to acetyl sulfide and alkali acetates. The acetyl sulfide is a very weak acid analog and slightly dissociated. Therefore, it was to have been expected that acetyl sulfide would show neutralization reactions only with metal acetates (such as silver and lead) whose sulfides ionize to an even lesser extent than $(\text{CH}_3\text{CO})_2\text{S}$.

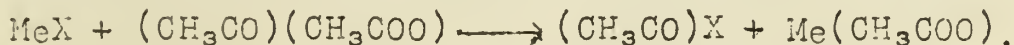
Mixed Acetic Anhydrides: Williams, Dickert, and Krynitsky (12) first demonstrated that mixed acetic anhydrides could be prepared; Jander showed that these compounds behave as acid analogs, undergoing neutralization reactions as illustrated by the following equation:



It was also found that benzenesulfonic anhydride in acetic anhydride exhibits characteristics of an acid analog, but only if allowed to react with a strong base analog, as, for instance, an alkali acetate.

REACTIONS OF SOLVOLYSIS IN ACETIC ANHYDRIDE (4)

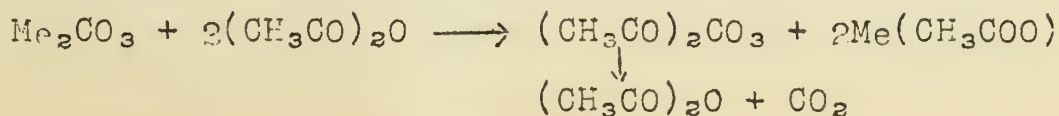
The reaction of solvolysis which occurs when certain metal salts and acidic chlorides are dissolved in acetic anhydride further substantiate the dissociation scheme proposed by Jander,



Although reactions of certain salts with acetic anhydride have long been known and recorded in the literature (13, 14), Jander undertook a further investigation of such phenomena from the point of view of solvolysis. It was found that some of their reactions were suitable for the preparation of metal acetates.

Solvolytic of Metal Salts:

1) Carbonates:



The diacetyl carbonate, being unstable, decomposes into the solvent and CO_2 , the formation of which is regarded as evidence of solvolysis. The extent of solvolysis depends both on the solubility of the salt in acetic anhydride and also the strength of the metal acetate formed as a base analog.

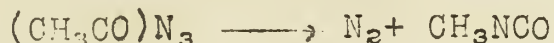
2). Sulfitcs: Only sodium and potassium salts were investigated; they react to give the metal acetate and SO_2 .

3). Sulfides: The sodium salt was found to react quantitatively, copper, lead, arsenic (III), antimony (III) and bismuth (III) sulfides, incompletely.

4). Nitrites: Sodium, potassium, silver, and barium salts were investigated, all showing complete solvolysis, yielding the acetate and NO , N_2 , and CO_2 (?). The reaction mechanism was not investigated further because of complicating side reactions.

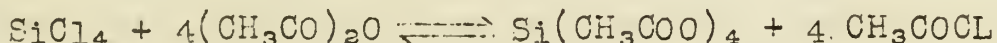
5) Halides: Being difficultly soluble, halides were not generally reactive, exceptions being HgF_2 (13), AlCl_3 (14), and sodium and potassium iodides.

6) Azide: The unstable acetyl azide formed first decomposes readily into N_2 and methyl isocyanate:

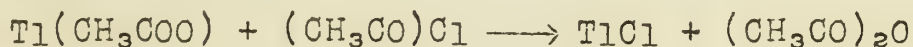


Solvolysis of Acidic Halides: Such compounds usually undergo some solvolysis to form the acetyl halide as one of the products. By adding thallium (I) acetate to remove the acetyl halide, it was found possible in some cases to bring about complete solvolysis. This procedure affords a good method for the preparation of acetates of certain elements.

1) Silicon Tetrachloride:



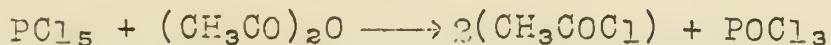
By adding thallium (I) acetate to effect the removal of the acetyl chloride, the reaction was made to go to completion. The thallium (I) acetate undergoes a neutralization reaction with acetyl chloride in accordance with the equation:



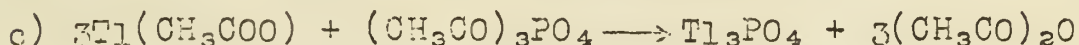
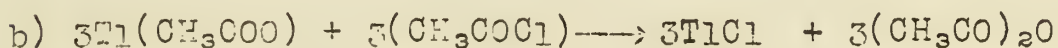
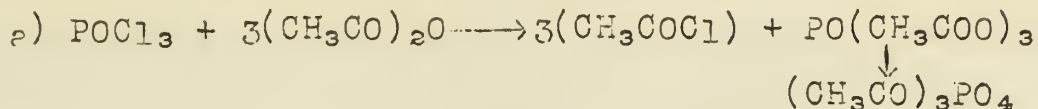
2) Germanium tetrachloride: Germanium tetra-acetate was prepared in a similar manner in almost quantitative yields.

3) Stannic Halides: Solutions of stannic chloride were not stable due to a secondary reaction with the solvent. With stannic bromide and iodide, however, thallium (I) acetate again caused complete reaction, giving high yields of tin tetra-acetate. Both the germanium and tin compounds are hydrolyzed readily by moisture in the air. Both are soluble in organic solvents.

4) Phosphorus Pentachloride: Earlier work had indicated that PCl_5 would solvolyze to the extent of forming POCl_3 , thought to be stable, as in the equation:



Jander, however, showed that further reaction did occur. From observations based on the amount of thallium (I) acetate used, the following reaction mechanism was proposed:



5) Arsenic, Antimony, and Bismuth Trichlorides: Arsenic trichloride is solvolyzed to the extent of 65% upon reaction with the pure solvent, while antimony and bismuth trichlorides do not react under similar conditions. Complete solvolysis was observed in all three cases when the solutions were treated with thallium (I) acetate.

ELECTROLYSIS IN ACETIC ANHYDRIDE (5)

In order to demonstrate that solutes in acetic anhydride solutions are actually ionized as in other non-aqueous solvents, Faraday's Law was checked for certain solutions. The only previous work covering electrolysis in acetic anhydride was carried out by Fichter and Stern (15), who obtained a silver iodide precipitate on a silver cathode from an acetic anhydride solution of an I (III) compound.

Cathodic Metal Deposition: The choice of metal salts was somewhat limited, the requirement being that the salt must be rather soluble, well dissociated, and must form only soluble acetates on solvolysis. About the only possibilities were some of the Group V trihalides, HgBr_2 , CoI_2 , and thallium(I) acetate. (The alkali acetates themselves were not suitable because of indefinite secondary reactions at the cathode.) Electrolyses of the following salts were attempted

1) Thallium (I) Acetate: A deposit of thallium metal was formed on the platinum cathode, but in yields of only about 25%. The low yield was attributed in part to reaction of the metal with the diacetyl peroxide formed at the anode (16). Also, a separate experiment showed that thallium metal reacts with the solvent itself, reforming thallium (I) acetate.

2) Mercury (II) Bromide: A saturated solution of HgBr_2 was electrolyzed with a platinum cathode and a silver anode. Subsequent experiments showed that the deposited mercury reacted with HgBr_2 to form practically pure Hg_2Br_2 , the yield being about 0.90 equivalents/Faraday.

3) Halides of Bismuth, Arsenic and Antimony: Only the bromide of bismuth gave a metal deposit. Arsenic trichloride and

[The text on this page is extremely faint and illegible. It appears to be a multi-paragraph document, possibly a letter or a report, with several lines of text visible across the page. The content is too blurry to transcribe accurately.]

tribromide and antimony trichloride were found to give small amounts of metal. Antimony tribromide, though, gave results ranging from 0.95 to 1.03 equivalents/Faraday, very close to the theoretical value.

The addition of KCl to an SbCl_3 solution was found to give a better conducting solution from which the metal was deposited in yields corresponding to 0.93 to 0.97 equivalents/Faraday. The formation of a soluble complex of the empirical composition $3\text{SbCl}_3 \cdot 2\text{KCl}$ is assumed.

Reactions of Anions: Only halides were examined, and the halogen was determined indirectly as the silver halide after electrolysis using a silver anode. The chlorides proved most satisfactory for checking Faraday's Law, although some good results were obtained with a few bromides and an iodide. A summary of the results is given in Table II.

TABLE II

| <u>Salt Electrolyzed</u> | <u>% Found of Theoretical Halogen Deposition</u> |
|------------------------------|--|
| ZnCl_2 | 95.4 |
| AsCl_3 | 90.5 |
| SbCl_3 | 100.1 |
| BiCl_3 | 95.6 |
| $\text{SbCl}_3 + \text{KCl}$ | 102.2 |
| $\text{AsCl}_3 + \text{KCl}$ | 106.4 |
| $(\text{CH}_3)_4\text{NOl}$ | 99.5 |
| MgBr_2 | 102.3 |
| ZnBr_2 | 101.5 |
| SnBr_4 | 99.1 |
| CoI_2 | 102.0 |

BIBLIOGRAPHY

- (1) Luder, W.F., Chem. Rev. 27, 547-80 (1940).
- (2) Cady, H.P. and Elsey, H.M., J. Chem. Ed. 5, 1425 (1929).
- (3) Jander, G., Rusberg, E., and Schmidt, H., Z. anorg. Chem. 255, 233-52 (1948).
- (4) Jander, G., Schmidt, H., and Blohm, C. Angew. Chem. A59, 233-7 (1947).
- (5) Jander, G., Schmidt, H., and Wittkopf, Z. anorg. Chem. 256, 113-25 (1943).
- (6) Jander, G., Naturwiss. 32, 139-78 (1944).
- (7) Shaw, L.I., J. Phys. Chem. 17, 132 (1913).
- (8) Franzen, H., Ber. 41, 3641-4 (1908).
- (9) Tsakalotos, D.E., Bull. soc. chim. (4), 7, 461-4 (1910).
- (10) Walton, J.H., and Withrow, L.L., J. Am. Chem. Soc. 45, 2689 (1923).
- (11) Hawthorne, J., J. Chem. Soc., 1906, 556.
- (12) Williams, J.W., Dickert, Y.J., and Krynitsky, J.A., J. Am. Chem. Soc. 45, 2689 (1923).
- (13) Ruff, O., and Bahlau, G., Ber. 51, 1758 (1918).
- (14) Adrianowsky, A., Ber., 12, 688 (1879).
- (15) Fichter and Stern, Helv. chim. acta, 11, 1256 (1928).
- (16) Glasstone and Hickling, J. Chem. Soc., 1936, 820.

R. L. Dalton

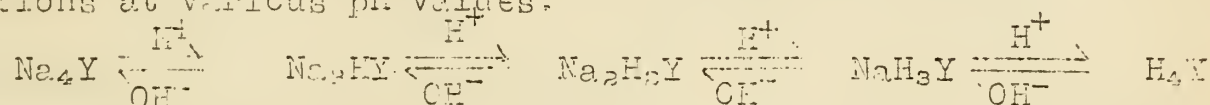
October 11, 1949

Introduction

The chelate complexes formed by alpha amino acids with a number of metals are known to be quite stable and have been the subject of considerable research. A rather recent development has been the synthesis and study of various polycarboxylic alpha amino acids, principally ethylenediaminetetraacetic acid. This acid is unique in that it has four carboxyl groups and two amino nitrogens thereby being capable of acting as a sexadentate group with the formation of 3 five-membered chelate rings. It is also of considerable interest because it forms stable complexes with the alkaline earth metals, whereas generally the complexes in which nitrogen is coordinated to an alkaline earth atom are very unstable.

Ethylenediaminetetraacetic Acid

Ethylenediaminetetraacetic acid (H_4Y) undergoes the following reactions at various pH values:



When there are two or more protons in the molecule, the structure is that of a zwitter or dipole ion. The two protons on the nitrogen atoms have an acidifying influence on the two protons remaining on the carboxyl groups. The ionization constants of the acid are $K_1=10^{-2}$, $K_2=2.1 \times 10^{-3}$, $K_3=6.9 \times 10^{-7}$, and $K_4=5.5 \times 10^{-11}$ (1).

Complex Formation

Ethylenediaminetetraacetic acid reacts with a large number of metals to give stable complexes. The following is a list of complex compounds that have been prepared and analyzed:

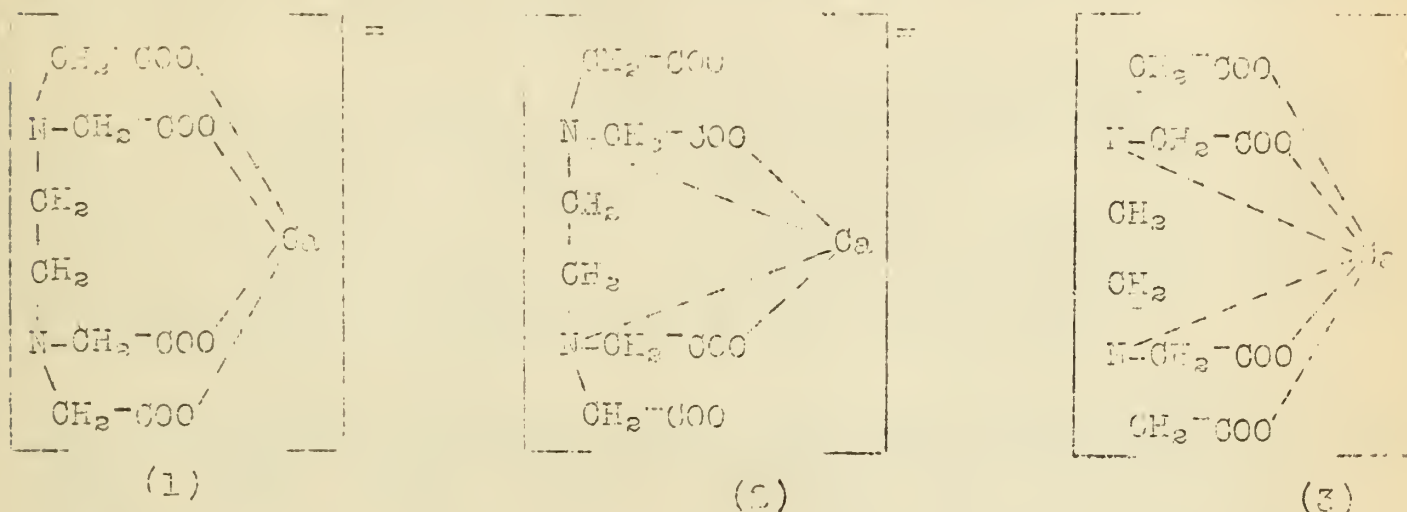
| | | Ref. | | | Ref. |
|--------------------------|---------------------------|------|-------------------------------------|--------------|------|
| $H_2 [CuY]$ | deep blue | (2) | $Ba [BaY] \cdot 2\frac{1}{2} H_2O$ | | (4) |
| $H_2 [NiY]$ | deep blue | (2) | $H_2 [SrY] \cdot 3\frac{1}{2} H_2O$ | | (4) |
| $Na_2 [CuY] \cdot 4H_2O$ | bluish-green | (3) | $Sr [SrY] \cdot 5 H_2O$ | | (4) |
| $Cu [CuY] \cdot 4H_2O$ | blue with violet tinge | (3) | $Na [CoY] \cdot 4 H_2O$ | red-violet | (5) |
| $K_2 [MgY]$ | | (3) | $H [CrY]$ | dark-violet | (5) |
| $Cd [CdY] \cdot 4 H_2O$ | | (4) | $H [FeY]$ | gold-yellow | (5) |
| $Zn [ZnY]$ | | (4) | $NH_4 [FeY] \cdot H_2O$ | yellow-brown | (5) |
| $Mn [MnY] \cdot 9 H_2O$ | | (4) | $K_2 [SrY] \cdot 4\frac{1}{2} H_2O$ | | (6) |
| $H_2 [HgY] \cdot H_2O$ | | (4) | $K_2 [BaY] \cdot 8 H_2O$ | | (6) |
| $H [BiY]$ | | (4) | $K_2 [CaY]$ | | (6) |
| $H_2 [BaY] \cdot 4 H_2O$ | | (4) | | | |

Attempts to prepare other complexes have resulted in the following salts:

| | | |
|----------------------------------|-------------------|------|
| $(UO_2)H_2Y \cdot H_2O$ | lemon-yellow ppt. | Ref. |
| $BeH_2Y \cdot 3\frac{1}{2} H_2O$ | | (2) |
| $Be_2Y \cdot 4\frac{1}{2} H_2O$ | | (4) |
| $Y_4Y_3 \cdot 24H_2O$ | | (4) |
| $Pb_2Y \cdot H_2O$ | | (4) |
| $HLaY$ | | (5) |
| $HNdY$ | | (5) |
| $ThY \cdot 2 H_2O$ | | (5) |
| UY | | (5) |

Only a limited number of the above complexes have been studied in an attempt to determine their properties and structure. Klemm and Raddatz (7,8) have studied the magnetic susceptibility of the complexes of Fe (III), Co (III), Cr (III), and Ni (II). They found the Ni complex to be paramagnetic and concluded that it is a tetrahedral penetration complex. The Co complex was found to be a penetration complex, but the measurements on the Fe and Cr complexes could not be used to distinguish between a penetration complex and a normal complex.

Considerable work has been done in an attempt to determine the structure of the Ca complex. Three structures have been proposed

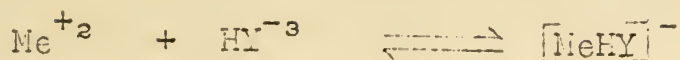


The first work along this line was done by Pfeiffer and Simons (6). They thought the second structure was the correct one, and so they sought to determine the significance of the ethylene bridge and the extra carboxyl groups by preparing other amino acid complexes of calcium. They found that $\text{HN}(\text{CH}_2\text{COOH})_2$ gave only a normal acid salt with Ca, while $\text{MeN}(\text{CH}_2\text{COOH})_2$ gave a weak complex. From this they concluded that for complex formation the two nitrogens must be tertiary and that ring closure through the ethylene bridge has a stabilizing influence. The fact that $\text{Me}_2\text{NCH}_2\text{COOH}$ did not form a complex was evidence to them that the "extra" carboxyl groups were essential for complex formation and therefore the structure of the complex must be number three above. Pfeiffer and Simons attempted to prove this by separation of the optical isomers which should exist, but were unsuccessful.

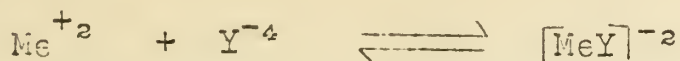
Schwarzenbach and Ackermann (1) found that the alkaline earths formed intermediate complexes of the type $[\text{CaHY}]^-$ and the more stable $[\text{CaY}]^{2-}$. The latter complexes have slightly acid properties, indicating formation of complexes of the type $[\text{Ca}(\text{OH})\text{Y}]^{2-}$. Schwarzenbach concludes that the ethylenediaminetetraacetate ion does not occupy all six coordination positions of the central atom, but that some of these are filled by water. The equilibrium formation constants for complexes of ethylenediaminetetraacetic acid and the alkaline earth metals at 20° C. are as follows:

| | $\log K_1$ | $\log K_2$ |
|----|------------|------------|
| Hg | 2.28 | 8.69 |
| Ca | 3.51 | 10.59 |
| Sr | 2.30 | 8.63 |
| Ba | 2.07 | 7.76 |

K_1 is the equilibrium constant for the reaction:



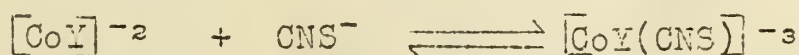
and K_2 is the equilibrium constant for the reaction:



An indication of the stability of these complexes is given by the fact that a Na_4Y solution will dissolve metal precipitates such as $\text{Ca}_3(\text{PO}_4)_2$, HgCO_3 , CaC_2O_4 , and BaSO_4 which normally have maximum insolubility in basic solutions.

In their attempts to decide among the three suggested structures for the Co complex, Martell, Plumb and Bergworth (9) eliminated the first one by the reasoning that, since the addition of Ca(II) to a solution of $\text{Na}_2\text{H}_2\text{Y}$ causes a drop in pH, the nitrogen atoms must be involved in complex formation, thereby releasing the protons. Titration curves of ethylenediaminetetraacetic acid in the presence of Ca(II) are interpreted as indicating that all four carboxyl groups are coordinated to the central atom.

Schwarzenbach (10) has shown that the chelate complexes of many divalent and trivalent metals show weak coordination unsaturation. $[\text{AlY}]^{-}$, $[\text{FeY}]^{-}$, $[\text{CrY}]^{-}$, and $[\text{InY}]^{-}$ take up an hydroxyl ion in the pH range 5-9, forming the corresponding hydroxocomplex $[\text{M(OH)Y}]^{-2}$. The complexes of the divalent metals do the same at a pH of 11. The resulting color changes indicate that a change in the coordination sphere has taken place. Other groups such as CNS^{-} , NH_3 , CN^{-} , and ethylenediamine can be added instead of OH^{-} . That these changes are not simple replacement of the ethylenediaminetetraacetate to give the ordinary ammino, thiocyanato, and cyanato complexes, is evident from the fact that different color changes would be expected. Schwarzenbach used extinction measurements to study the reaction of pale violet $[\text{CoY}]^{-2}$ and thiocyanate and found the following addition took place:



The equilibrium constant was found to be

$$K = \frac{[\text{CoY(CNS)}]^{-3}}{[\text{CoY}]^{-2} [\text{CNS}^{-}]} = 0.7$$

indicating that the product is an unstable complex. He compares this with the formation of $[\text{Co(CNS)}_4]^{-2}$ and concludes that in both cases the thiocyanate ion replaces a water molecule in the coordination sphere of the cobalt. Therefore the Co complex has the formula $[\text{CoY(H}_2\text{O)}]^{-2}$. On the other hand, Co(III) gives a complex $[\text{CoY}]^{-}$ which evidently contains no water since the anion shows no acid character and no other groups will enter the complex as with $[\text{CoY}]^{-2}$. Further proof that the ethylenediaminetetraacetate ion occupies all six coordination positions around the Co(III) is given by the complexes $[\text{CoYL}]^{-2}$ which are thermodynamically unstable. (L may be Br^{-} , OH^{-} , or NO_2^{-} .) These complexes occur as intermediates when $[\text{CoY}]^{-2}$ is oxidized with Br_2 , NO_2 , or H_2O_2 . The $[\text{CoY}]^{-}$ complex is neither acidic nor basic and is stable over the pH range 0-13, but

the complex is destroyed by strong acid or alkali. Schwarzenbach was unable to replace the Br^- in $[\text{CoYBr}]^{-2}$ by other groups such as NH_3 , ethylenediamine, or acetate.

Applications

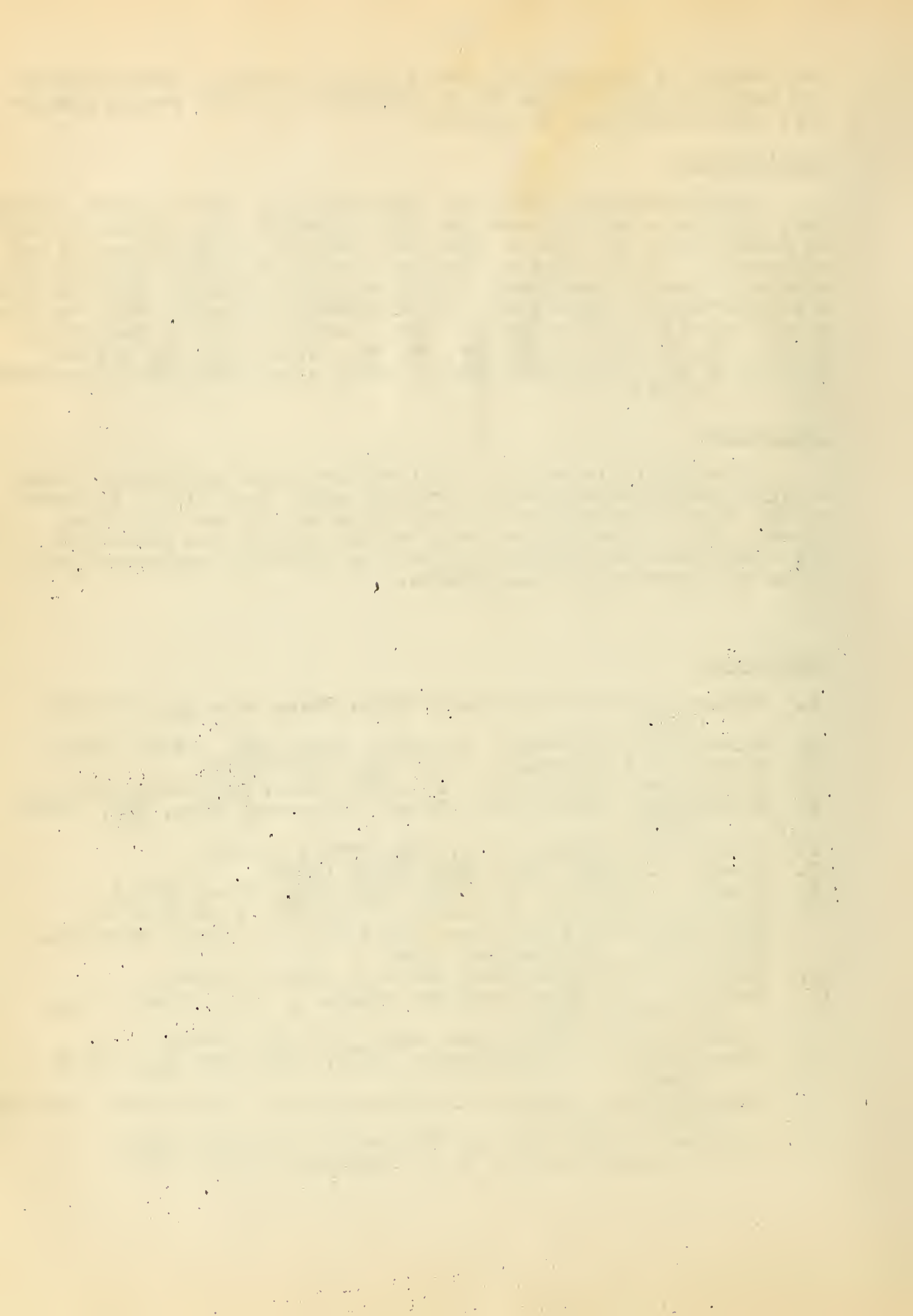
Ethylenediaminetetraacetic acid was first used in water softening; it forms a soluble complex with the metal ion. It may be used to remove deposits such as CaSO_4 and alkaline earth carbonates and phosphates. It may also be used to prevent reactions catalyzed by metals by forming complexes with those metals (9,15). Schwarzenbach has investigated the use of ethylenediaminetetraacetic acid for the quantitative determination of a large number of metals including: Al, Ca, Cd, Co, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Zn, Sr, Ce, and Li. Procedures for determining many of these metals have been described (11, 12, 13, 14).

Conclusion

Although the industrial applications of the complexing action of ethylenediaminetetraacetic acid are many, very little is known of the chemical properties and structure of the complexes thus formed. It is apparent that many of the studies are incomplete, and conclusions are frequently based on limited experimental results and questionable assumptions.

References

1. Schwarzenbach and Ackermann: *Helv. Chim. Acta* 30, 1798-1804 (1947).
2. Brintzinger and Hesse: *Z. anorg. Chem.* 249, 113-18 (1942).
3. Pfeiffer and Offermann: *Ber.* 75B, 1-12 (1942).
4. Brintzinger and Munkelt: *Z. anorg. Chem.* 256, 65-74 (1948).
5. Brintzinger, Thiele, and Müller: *Z. anorg. Chem.* 251, 285-94 (1943).
6. Pfeiffer and Simons: *Ber.* 76B, 847-55 (1943).
7. Klemm: *Z. anorg. Chem.* 252, 225-6 (1944).
8. Klemm and Raddatz: *Z. anorg. Chem.* 250, 204-6 (1942).
9. Martell, Plumb, and Bersworth: "Properties and Uses of Ethylenediamine Tetra Acetic Acid and Its Salts," Bersworth Chemical Co., Framingham, Mass.
10. Schwarzenbach: *Helv. Chim. Acta* 32, 839-53 (1949).
11. Biedermann and Schwarzenbach: *Chemia* 2, 56-9 (1948). *C.A.* 42, 3694 (1948).
12. Schwarzenbach: *Helv. Chim. Acta* 29, 1338 (1946).
13. Schwarzenbach and Biedermann: *Helv. Chim. Acta* 31, 459-65 (1948).
14. Schwarzenbach, Biedermann, and Bangerter: *Helv. Chim. Acta* 29, 811-18 (1946).
15. Technical Bulletin No. 1, "The Modern Chelating Agent," Bersworth Chemical Co., Framingham, Mass., 1949.



RECENT DEVELOPMENTS IN THE CHEMISTRY OF META- PYRO- AND POLYPHOSPHATES

Emil W. Grieshaber

October 18, 1949

Within recent years the use of compounds derived from the oxy-acids of phosphorous has increased tremendously in widely differing industries. Random examples covering the use of metaphosphates to stabilize supersaturation and to soften water, of orthophosphates in fertilizers and in metal surface treatment, of pyrophosphates in soap powders, in well drilling muds, in dye baths, and as dispersing agents in cold water paints (3, 11) may be cited to illustrate some of the many fields in which these compounds are employed and may give an indication of the large amounts consumed annually. A natural consequence of increased production has been increased interest in the properties and structural characteristics of these materials. Great advances have been made in explaining past empirical findings. This progress has been based on what is known of the configurations and structures of these compounds. The object of this seminar is to describe two recent pieces of research which add to our knowledge in this field of chemistry.

The following table is included to indicate the configuration of some of the compounds to be discussed.

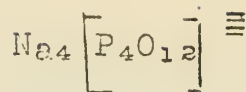
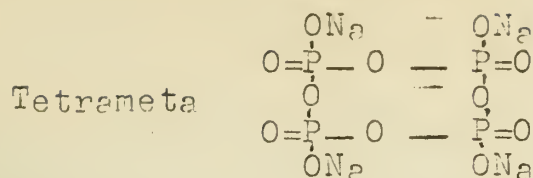
Table I

Configurations of Poly- and Metaphosphates (1,9)

| | <u>Classical</u> | <u>Werner</u> | <u>Crystal Structure</u> |
|----------|--|--|---|
| Ortho | $\begin{array}{c} \text{ONa} \\ \\ \text{NaO}-\text{P}=\text{O} \\ \\ \text{ONa} \end{array}$ | $\text{Na}_3 + [\text{PO}_3]^-$ | $\begin{array}{c} \text{O} \\ \\ \text{O}-\text{P}-\text{O} \\ \\ \text{O} \end{array}$ <p>All O's alike P-O=1.54Å</p> |
| Pyro | $\begin{array}{c} \text{ONa} \\ \\ \text{NaO}-\text{P}=\text{O} \\ \\ \text{O} \\ \\ \text{NaO}-\text{P}=\text{O} \\ \\ \text{ONa} \end{array}$ | $\text{Na}_4 + [\text{P}_2\text{O}_7]^{2-}$ | $\begin{array}{c} \text{OOO} \\ \diagdown \quad \diagup \\ \text{P} \\ \\ \text{O} \\ \\ \text{P} \\ \diagup \quad \diagdown \\ \text{OOO} \end{array}$ <p>Six O's alike One different P-O = 1.56Å P-O' = 1.52Å</p> |
| Tri-poly | $\begin{array}{c} -\text{ONa} \\ \\ \text{NaO}-\text{P}=\text{O} \\ \\ \text{O} \\ \\ \text{NaO}-\text{P}=\text{O} \\ \\ \text{O} \\ \\ \text{NaO}-\text{P}=\text{O} \\ \\ \text{ONa} \end{array}$ | $\text{Na}_5 + [\text{P}_3\text{O}_{10}]^{3-}$ | |
| Tri-meta | $\begin{array}{c} \text{ONa} \\ \\ \text{O} \diagdown \quad \diagup \text{O} \\ \quad \quad \\ \text{NaO}-\text{P}=\text{O} \quad \text{O}=\text{P} \\ \quad \quad \\ \text{O} \diagup \quad \diagdown \text{O} \end{array}$ | $\text{Na}_3 + [\text{P}_3\text{O}_9]^{3-}$ | |

Classical

Werner



It may be noted that both linear and cyclic types of metaphosphates can exist; it must be borne in mind constantly that pentavalent phosphorus in phosphates exhibits a tetrahedral configuration; (12) the chain-like compounds diagramed above are not planar. The specific P-O- distances and P-O-P bond angle will be taken up in part II.

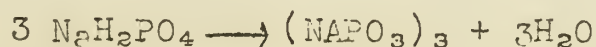
I

The literature contains a confusing number of formulas for metaphosphates. If $(\text{HPO}_3)_n$ be taken as the general formula examples of salts in which n may vary between 2,3,4,5,6,8,10, and 14 are cited in the literature (2,4). The general methods of determining the molecular weights of salts of such compounds (i.e. 1. Freezing-point lowering in water and 2. The Ostwald-Walden-Bredig rule) have been criticized by Davies and Monk as being unsatisfactory (2). These methods have been applied to the sodium salts with the primary object of determining the valency of the anion. The freezing point lowering procedure is subject to error because of the possibility of complex formation and ion-association in all electrolytes, especially those where polyvalent ions may exist.

The Ostwald rule is somewhat empirical in character; the difference between the equivalent conductance of an electrolyte at N/32 and N/1024 divided by ten gives approximately the product of the ionic valences (e.g. 2 for MgCl_2 and 4 for MgSO_4 or $\text{Na}_4\text{P}_2\text{O}_7$) (5,9). However, this rule has not been applied successfully even to orthophosphates, let alone polyvalent electrolytes and those containing ions of high molecular weight (2,9).

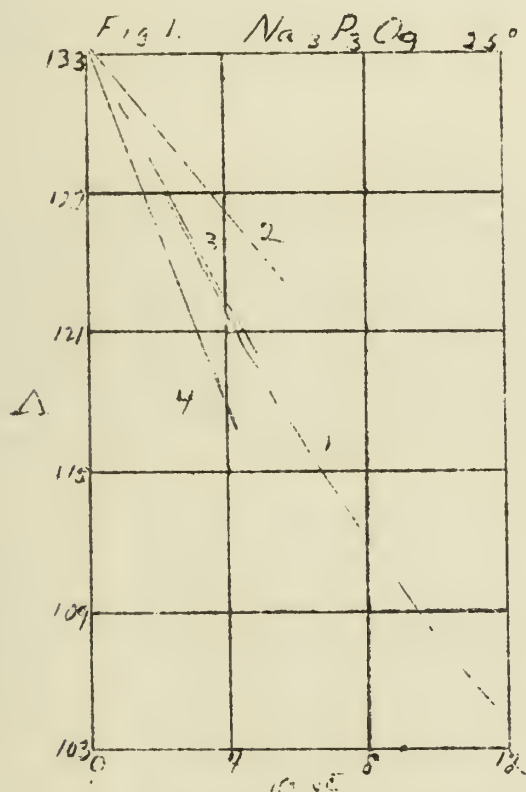
As a result of the work of Davies and Monk the metaphosphates have been found to exhibit only three degrees of polymerization (2,7,8). In terms of the formula $(\text{NaPO}_3)_n$ these polymers exist for $n = 3, 4$ and approximately 100. In view of the errors encountered in the valency type determinations above, the procedure employed by Davies and Monk is interesting. First, conductivity measurements were carried out with highly dilute solutions of the sodium salts to determine if the dissociation is normal. If no drift in conductivity values with time was observed the salt was considered stable towards water. Next, the conductivity of the corresponding acid was measured and dissociation constants calculated; this showed to what extent the sodium salts were affected by hydrolysis and further characterized the anion.

The first compound investigated was sodium trimetaphosphate and was prepared by heating primary sodium phosphate in a platinum crucible.

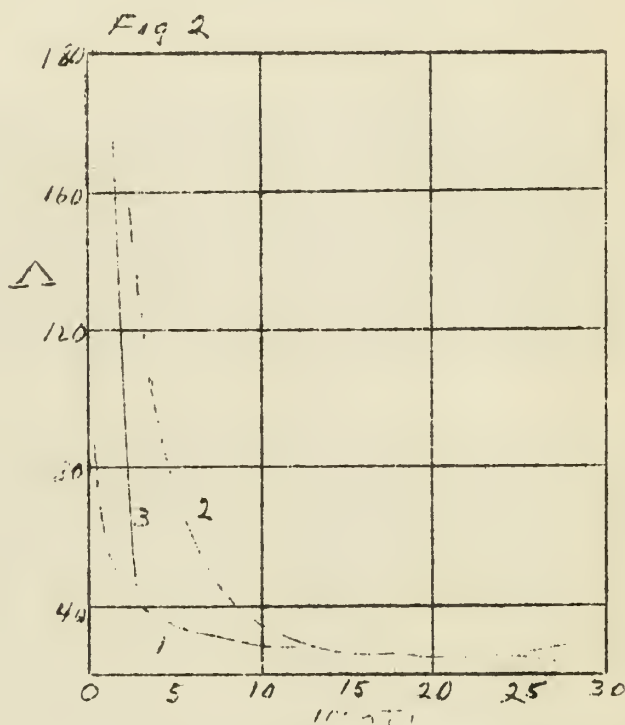


The corresponding acid was prepared by passing the sodium salt through a column of a cation-exchange resin. Its dissociation constant is approximately $K = 9 \times 10^{-3}$.

Typical results are shown in Fig. 1. Equivalent conductivity is plotted against the square root of the concentrations $\Lambda_0 = 133.70$ and after deduction of 50.11 for the mobility of the sodium ion the mobility of the metaphosphate ion becomes 83.59. Fig. 1 also shows the theoretical limiting slopes calculated from Onsager's equation for the possible salts $\text{Na}_2\text{P}_2\text{O}_6$, $\text{Na}_3\text{P}_3\text{O}_9$, and $\text{Na}_4\text{P}_4\text{O}_{12}$. Experimental agreement with the second of these is strong evidence that the anion is trivalent. By an exactly similar procedure sodium tetrametaphosphate was found to give values in close agreement with those calculated for a uni-tetavalent electrolyte. This salt was prepared by the method of Warschauer from $\text{Cu}(\text{H}_2\text{PO}_4)_2$ (13). The values for the corresponding acid dissociation constants are given as $K_3 = 2.7 \times 10^{-7}$, $K_4 = 2.4 \times 10^{-10}$.



1. Experimental curve
- 2, 3, 4. Onsager limiting slopes for 1-2 valent, 1-3-valent and 1-4-valent salts respectively.



1. Sodium "hexametaphosphate"
2. Octadecylamine hydrochloride
3. "Hexametaphosphoric" acid.

The problem of establishing the molecular weight of the higher polymers of the metaphosphates is more complex. Derivatives are of doubtful value; an ultracentrifuge does not give conclusive results, and it is difficult to obtain and establish purity (6). One would predict this state of affairs from the knowledge that the polymetaphosphates are formed in chains of apparently widely varying length. As a result, any determination would give a value which is the average for all of the species present under the conditions of the determination. Thus an ultracentrifuge would give a distribution value for the various aggregates present.

The conductivity curves obtained by Monk showed no relation to that of a normal salt and the slope was far steeper than would be calculated for a uni-hexavalent salt. The conclusions drawn are in favor of a high value for n and definitely against the existence of a "hexametaphosphate" as was formerly believed.

Methods of preparation presumed to give dimeta- and monometaphosphates have been found in error. The former compound was found to be the trimetaphosphate; the latter, a mixture of trimeta- and polymetaphosphates. It thus seems established on the basis of these studies that metaphosphates may exist as polymers in rings of 3 or 4 units (six and eight membered rings) or in very long chains of colloidal dimensions.

Further work by these authors confirmed the fact that the fusion of equimolecular amounts of $\text{Na}_4\text{P}_2\text{O}_7$ and any sodium metaphosphate gives sodium tripolyphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$, as the only stable compound. In this case the difficulty of obtaining a pure compound did not allow an accurate check on the theoretical calculations as in earlier instances. It should be pointed out, however, that the preparative difficulty is not met with in the commercial preparation of the tripolyphosphate.

II

It has long been known that rapid quenching on any melt having an $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ ratio between 1:1 and 5:3 will yield a glassy metaphosphate. Besides the well known ability to "sequester" polyvalent cations these compounds have been found to stabilize supersaturation of calcium carbonate solutions. This latter property has been the subject of recent investigation by Reistrick. The same investigator has also used X-ray diffraction technique in the study of the structure of hypophosphoric acid, $\text{H}_4\text{P}_2\text{O}_6$ (10).

Reistrick attacked the problem of stabilization of supersaturation of calcium carbonate by first studying the crystal structure of the calcite. He showed that the polymetaphosphate chain could be superimposed on the calcium ion layer and that dimensions were such as to fit the lattice readily. The P-O-P bond angle is considered to be approximately 141° because it permits the center of charge of every PO_4 group to approach as closely as is possible to the layer of calcium ions while still retaining these centers immediately above the centers of the equilateral triangles formed by the calcium ions. The polymetaphosphate chain can then be imagined as winding its way over the calcite surface. Once it was established that the metaphosphate could fit the lattice it was then postulated that as a calcite crystal began its growth a polymetaphosphate grouping could attach itself to the surface and decrease the electrostatic potential to such an extent that further growth at that surface was stopped. Repeated over all of the surfaces of a nucleus this phenomenon would prevent growth to particles large enough to precipitate. And indeed, solutions treated in this way remain clear for weeks.

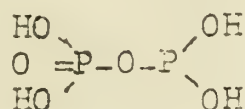
Nitrate and iodate ions will also fit the lattice but their single charge as compared to the spaced out multiple charges of the polymetaphosphate apparently makes them unable to compete with the carbonate ion during crystal growth.

In support of Reistrick's theory two important facts were observed: 1. Compounds with spaced out charges (i.e. sodium triphosphate and tetrasodium pyrophosphate which also fit the calcite lattice

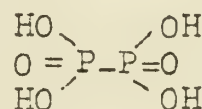
showed the same supersaturation stabilization while

2. Compounds with soaced out charges which did not fit the lattice (i.e. (a) cyclic sodium trimetaphosphate and tetrametaphosphate and (b) sodium metasilicate, trilon A and B) did not stabilize the supersaturation.

As an incidental result of these investigations it was possible to shed some light on the structure of hyponphosphoric acid, $H_4P_2O_6$. Structures I and II were considered possible even after X-ray studies although such an investigation did favor structure II. The fact that $H_4P_2O_6$ showed no ability to stabilize supersaturation was offered as added proof in favor of structure II since I with its P-O-P linkage would have been expected to be an effective stabilizer.



I



II

Critique

It is apparent from the above discussion that the properties of a compound in solution are employed as evidence of the structure of that compound in the solid state. Very long chains in metaphosphate glasses may be cleaved into random lengths upon solution. This fact must be borne in mind when the properties of a solution of such a glass are used to study its solid state. In other words, the value for n in solution may be only vaguely related to that for n in the solid state. At the same time, the value obtained for n in solution can give only an average of such a value which gives no indication of the upper and lower limits of the actual n in that solution.

Successful as the Raistrick theory appears to be, a further test is possible. This would involve testing a totally different lattice and a chain-type of molecule related to each other in a manner similar to the calcite and polymetaphosphate described above. Analogous results (i.e. stabilization of supersaturation) would definitely lend strength to the theory.

Bibliography

1. Andrieth and Hill, J. Chem. Ed., 25, 20 (1948)
2. Davies and Monk, J. Chem. Soc., 94, 413-22 (1949)
3. Easterwood, Ind. Eng. Chem., 34, 13-19 (1942)
4. Ephraim, Inorganic Chemistry, p. 623, Interscience Publishers Inc. (1947)
5. Glasstone, Physical Chemistry, p. 891, D. Van Nostrand Co. (1940)
6. Jones, Ind. Eng. Chem. Anal., 14, 536 (1942)
7. Monk, J. Chem. Soc., 95, 423-27 (1949)
8. Monk, *ibid.* 96, 427-29 (1949)
9. Quimby, Chem. Rev., 40, 141 (1947)
10. Raistrick, Unpublished report to Ann. Conv. of C.I.C. Halifax, May, 1949.
11. Schwartz and Munter, Ind. Eng. Chem., 34, 32 (1942)
12. Wells, Structural Inorganic Chemistry, p. 419, Oxford Press, (1947)
13. Warscheuer, Z. anorg. Chem., 36, 137 (1903).

M. Krulfeld

October 25, 1949

INTRODUCTION

Since the time of Sir Humphry Davy, who discovered sodium and potassium in 1807 by the electrolysis of the fused hydroxides of these elements, the electrolysis of fused materials has been of great importance from both the industrial and scientific point of view. Today the existence of large and growing industries, based on the production of aluminum and magnesium by electrolysis of high temperature melts, to name only the largest, is sufficient evidence of their importance. Relative to the value of these and similar processes, however, little work has been done on the electrochemistry of fused salts from the scientific point of view. For the most part this state of affairs can be ascribed to two factors: First, the difficulty of working with materials at fairly high temperatures under constant and reproducible conditions. Second, the difficulty of interpreting results and drawing useful conclusions from work done in media whose behavior is not adequately accounted for by theory. This difficulty is still with us. As a result of the above difficulties, most work on electrolysis is confined to studies of salts in solution, rather than to their melts. For the most part studies on the electrochemistry of fused salts consist of isolated papers. However, a few workers, notably Lorenz and his co-workers (1) early in this century, and more recently Drossbach in Germany and Hildebrand and his coworkers in this country, have produced a considerable body of work on the subject.

CONDUCTANCE IN FUSED SALTS

Conductance measurements are comparatively easy to make, yet, as indicated by Mantzell (2) as recently as 1943, data on this property are subject to large errors. In the following table, taken from Mantzell, are tabulated the values for a , b , and K in the equation $K = a + b(t - t_1) \times 10^{-3}$ where K is the specific conductance, a and b are constants, and t and t_1 are temperatures in degrees centigrade, as taken from the data of different workers.

TABLE I

| Salt | t_1 | Jager and Kapma | | Arndt et al. | | Biltz and Klemm | | Ryschke- witsch | |
|------|-------|--------------------|------|--------------|-----|--------------------|-----|--------------------|------------|
| | | a | b | a | b | a | b | a | b |
| NaCl | 850 | --- | --- | 3.5 | 3.2 | 3.66 | 2.2 | 3.77 3.44 | 5.1 3.8 |
| KF | 860 | 2.92 | 3.85 | 2.12 | 5.0 | --- | --- | 4.14 | 4.5 |
| KCl | 800 | 2.33 | 4.10 | 2.19 | 2.1 | 2.19 | 2.1 | 2.43 | 3.5 |

Values for a show variations up to 40% and of b shows variations up to 300%. The errors in b are probably due to difficulties in temperature measurement. Mantzell proposed a simple device for making crude conductance measurements, consisting of a trough of a very high-melting material of constant cross-section, with iron electrodes set into the ends. The melts can be poured into the trough to a definite height. When current is sent through the melt, the resistance can be found by applying Ohm's law to the current and voltage measurements. ρ , the specific resistance, equal to the reciprocal of K , can then be found by applying $R = \rho l/A$ where R is resistance, l is length, and A is cross-

sectional area of the melt. By this means Mantzell obtained fairly consistent values of K for the salts NaCl , KCl , and CaCl_2 , and for their mixtures. Plotting the values of K for the mixtures against the percent composition, he obtained straight isothermals, which indicated that the specific conductances of the mixtures were an additive function of the specific conductances of the pure components. However, possible errors up to 15% were noted in his measurements, which he could not explain.

In confirmation Kraus (3) says that for most salt mixtures conductance is very nearly an additive property, and takes that fact as evidence that little reaction usually takes place on mixing, an indication of a high degree of ionization in the melt.

Walden (4,5) and his co-workers did considerable work on fused salts particularly on the substituted ammonium picrates. Their work indicated that specific conductance could be related to molecular size. For a given degree of substitution, the larger the substituted group, the smaller the specific conductance. This can be seen in the following table.

| Table II | |
|--|----------------------|
| Salt | Specific conductance |
| $(\text{CH}_3)_2\text{NH}_2\text{Pi}$ | 0.019 |
| $(\text{C}_2\text{H}_5)_2\text{NH}_2\text{Pi}$ | 0.013 |
| $(\text{C}_3\text{H}_7)_2\text{NH}_2\text{Pi}$ | 0.009 |

The lowered mobility for larger ions is not surprising. It was further indicated, however, that the higher the degree of substitution, the higher the specific conductance. Thus $(\text{C}_2\text{H}_5)_3\text{NHPi}$ has a higher specific conductance than $(\text{C}_2\text{H}_5)_2\text{NH}_2\text{Pi}$. Walden explained this by assuming that the more highly substituted salts undergo a higher degree of dissociation in the melt.

Upon correlating his work on the viscosity and the conductance of highly alkylated ammonium picrates in the fused state, Walden obtained the following rules:

$$l_A = 4.032 / \eta \sqrt{M_A}$$

$$l_K = 3.17 / \eta \sqrt{M_K}$$

Where l_A and l_K are the mobilities of anion and cation respectively, η is the viscosity of the melt, and M_A and M_K are the ionic weights of anion and cation respectively. Among other less important restrictions, these rules are valid only on the assumption of highly dissociated ions and negligible solvation effects. For very large ions, such as those from highly alkylated ammonium picrates, the relationship was found to hold in solution as well as in the melt. When tested on several salts with smaller ions, it was found to hold approximately, but only in the melt.

However, Erdely-Gruz (6) pointed out several years later that the Walden relation does not appear to be valid for many molten salts, particularly just above their melting points. If we take $\lambda = l_A + l_K$, then the ratio $\frac{\lambda_{\text{experimental}}}{\lambda_{\text{calculated}}}$ will equal 1.0 wherever the Walden relation holds.

Some actual values are given below:

Table III

| <u>Salt</u> | $\frac{\chi_{\text{exp}}}{\chi_{\text{calc}}}$ |
|-------------------|--|
| LiNO ₃ | 1.05 |
| NaCl | 1.58 |
| AgCl | 2.16 |
| AgI | 4.22 |

At higher temperatures the abnormal ratios tend to decrease, but may still be well above 1.0 in value.

Since the Walden relation assumed complete or near-complete dissociation, Erdey-Gruz pointed out that ordinary electrolytic ion migration will not explain the very high conductances actually obtained. He therefore assumed that Grotthus conductivity, as well as ordinary ion migration, occurs in some fused salts. If this assumption is correct, it is possible that Grotthus conductivity occurs even in some cases where the Walden relation appears to hold, and that the apparent validity of the rule may be only accidental. Thus the assumption of complete dissociation based on the Walden rule may, at least in some cases, be in error.

A somewhat different approach to conductance has been taken by Bloom and Heymann (7). They found that for ionic salts the equation $K = \text{constant} \times e^{-C/RT}$ is valid, where K is specific conductance, R the gas constant, and T the absolute temperature. The value for C can be found by plotting $\log K$ versus $1/T$ and then finding C from the slope of the resulting straight line. C can be considered to be the activation energy of ionic migration. High values of C are obtained in cases where compound or complex formation occurs, as in PbCl₂ and KCl mixtures. Equivalent conductance values can be obtained from K values by the equation $\Lambda = KE/d$ where Λ is equivalent conductance, K is specific conductance, E is equivalent weight, and d is density.

Some interesting conclusions can be drawn from tabulated values such as the following:

Table IV

| <u>Salt</u> | Λ |
|-------------|-----------|
| LiCl | 133 |
| NaCl | 150 |
| KCl | 120 |
| LiBr | 177 |
| NaBr | 148 |
| KBr | 109 |

If we compare salts with the same cations but different anions, we see that the equivalent conductance changes very little. If we compare salts with the same anion but different cations, the equivalent conductance changes markedly. The indication is that for the above salts conduction is very largely by cationic transfer, with anionic transfer of much smaller importance. That is to say, if measurable, the transference number would be large for the cations, and small for the anions. Data on the alkaline earth and lead chlorides indicates that in the fused state these salts conduct largely by anionic transfer.

No transference number determination appears to have been made as yet. The attempts of Schwarz (8,9) to obtain such information by what amounts to a moving boundary method are instructive. He pointed out that the Hittorf method of determining transference numbers depends on having a solvent, such as water, which can be assumed to be unaffected by the current. No such solvent is available for fused salts. Schwarz proposed the use of electrodes of molten lead, with fused PbCl_2 and PbBr_2 or similar systems of two salts with one common and two dissimilar ions in his apparatus. After the passage of current, by chilling and then breaking up his solidified melt, and analyzing the different portions, he hoped to be able to follow the movement of the dissimilar ions relative to each other. Several attempts resulted in data of no value whatsoever. Schwarz attributed his failure very largely to convection currents set up in the fused salt system. Despite several attempts to overcome the difficulty, he failed. It is possible that other factors, such as the solubility of the fused salts in each other, also affected his results.

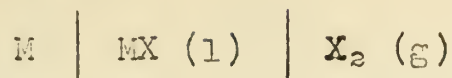
POTENTIALS IN FUSED SALT SYSTEMS

Drossbach (10,11,12,13,14,15) has published many papers on the subject of molten salts as electrolytes. For the most part he has been interested in processes and measurements of industrial and engineering importance, with only secondary interest in theoretical questions. His emphasis has chiefly been on determining the value of such things as the polarization potential for industrial processes. P is defined by the equation $P = U - IR$ where U is the overall voltage across the fused salt cell, I is the current, and R the resistance. The polarization potential is of particular importance in engineering because it permits the accurate calculation of the heat generated by a cell during electrolysis, allowing for efficient heat exchange design. Drossbach has pointed out, however, (11) that P is ordinarily not the same as the back emf of the cell, the difference arising because of various polarizing and depolarizing effects, such as the varying oxygen content of the melt, or the production of metallic "fog" at the cathode, which may diffuse through the melt to recombine again with anode products.

In several cases, notably that of BiCl_3 , Drossbach's studies have permitted the electrolytic recovery of pure metals from fused melts ordinarily considered to be difficult or impossible to electrolyze successfully.

Hildebrand and his co-workers, notably Salstrom, have carried out a long series of investigations (16,17, 18, 19, 20,21,22,23,24,25) on the thermodynamic properties of fused salts as determined by emf measurements of fused salt cells.

In a cell of the type



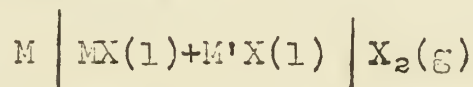
there is the overall reaction: $M + \frac{1}{2} X_2 = MX$. If the emf of such a cell is determined at a series of different temperatures, it is possible to obtain the free energy, the entropy, and the heat of formation of MX from the equations:

$$\Delta F^0 = -nEF$$

$$\Delta S^0 = 23070 \, n \, dE/dT$$

$$\Delta H^0 = \Delta F^0 + T\Delta S^0 = -nEF + 23070 \, nTdE/dT$$

And if the cell is now altered to



where M' is another metal, we will then have a solution of MX in M'X, at an activity a_1 and a mole fraction N_1 , and the emf will be changed also. From measurements of such a cell we can get:

$$\Delta F_1 = -nEF = RT \ln a_1$$

from which the activity a_1 can be found, as well as the activity coefficient $\gamma_1 = a_1 / N_1$ of component 1 in the melt.

Further, the free energy, entropy, and enthalpy of solution can be found from:

$$\bar{F}_1 = \Delta F_1 - \Delta F_1^0$$

$$\bar{S}_1 = \Delta S_1 - \Delta S_1^0$$

$$\bar{H}_1 = \Delta H_1 - \Delta H_1^0$$

And, for such melts, once we have found the activities of both components, we can plot such activities against the composition of the melt, obtaining a diagram which permits us to tell whether the melts are ideal or non-ideal, that is, if they do or do not follow Raoult's law.

Salstrom and Hildebrand accumulated such thermodynamic data for a large number of systems involving lead, silver, and zinc halides, dissolved in alkali halides and in each other. Attempts to get similar data for $CdCl_2$ failed on account of the development of a "fog" of cadmium metal in the molten salt and a consequent irregularity in the value of the emf.

The data for AgBr dissolved in molten alkali bromides, (22) indicated to Hildebrand and Salstrom a relationship between departures from ideal behavior of the solute and the mole fraction of the solvent molten salt which is illustrated in Figure 1 on the following page.

The data fits the straight lines very closely, and the curve is little affected by temperature. The following simple equation expresses the data:

$$\bar{F}_1 - \bar{F}_{1i} = RT \ln \frac{a_1}{N_1} = RT \ln \gamma = b N_2^2$$

where b is a constant depending on the particular molten solvent and solute. A negative slope indicates a negative deviation from ideality, and a positive slope a positive deviation from Raoult's Law in a very striking manner. Ideality, of course, would be shown by a value of zero for both $RT \ln$ and for b . Although A_8Br in the alkali bromides shows both negative and positive deviations, depending on the particular alkali in question, Salstrom later showed that A_8Br in $PbBr_2$ and A_8Cl in $PbCl_2$ show only very slight deviations. The system $PbBr_2$ in $ZnBr_2$, on the other hand, shows large positive deviations from ideality.

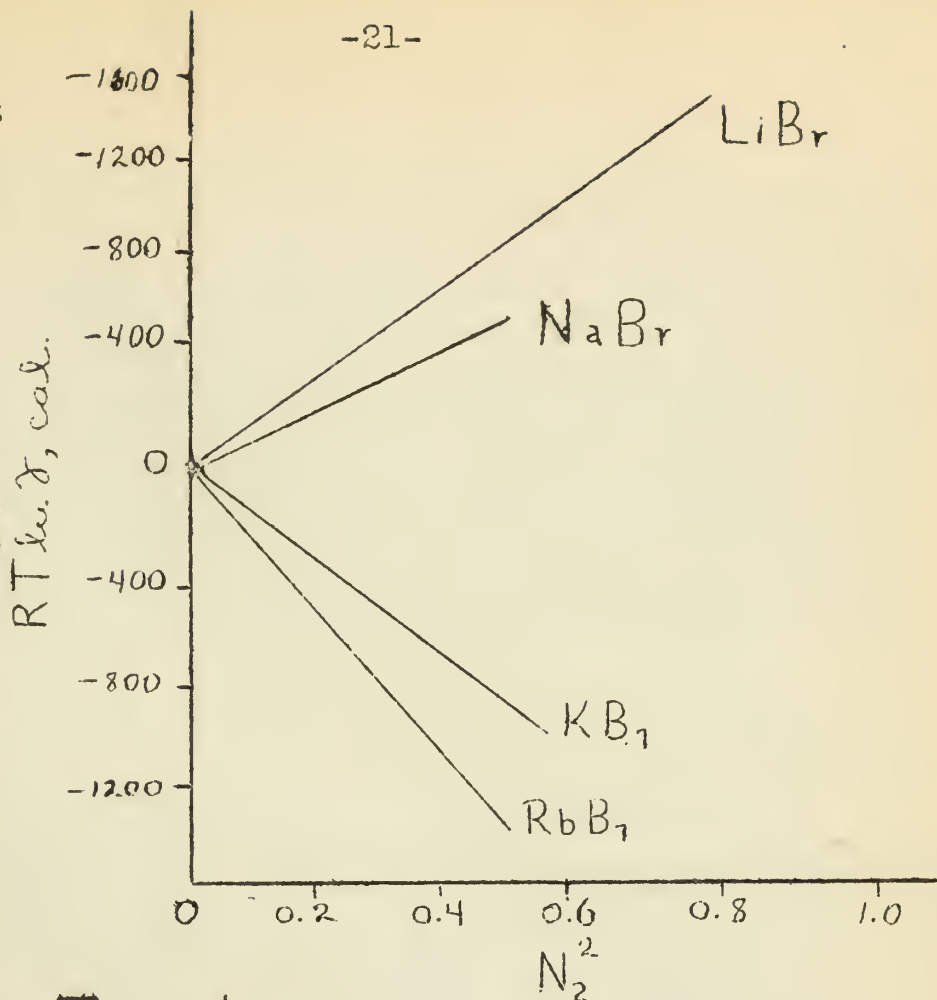


Fig. 1

Rose, Davis, and Ellingham (26) have recently obtained some data on the free energies and enthalpies of reduction for several chlorides, oxides, and sulphides. However, their results were obtained in an apparatus open to the atmosphere, and can not be considered very accurate.

OTHER ELECTROCHEMICAL PROPERTIES

While the work using conductance and potential measurements as indicated accounts for most of the studies on the electrochemical properties of fused salts, another approach has recently been taken by Hamer and Schrodt (27). They have investigated some of the possibilities of using molten electrolytes in a galvanic cell for the production of electricity. In particular they studied the cell:

Mg: solid or molten electrolyte: $MnO_2:C$

Various electrolytes were used: $NaOH$, KOH , $NaHSO_4$, $LiNO_3$, $NaNO_3$, $NaNO_2$, KNO_3 . Temperatures were varied from room temperature to well above the melting points of the electrolytes being tested. In general, the voltages of the cells at room temperature were near zero, rising slowly as the temperature rose. As the melting point approached the voltage rose sharply, reaching a value at the melting point which thereafter increased only slowly with temperature. In order to obtain sustained current, however, the melting point of the electrolyte had to be reached or exceeded.

$NaOH$ and KOH were by far the best electrolytes tested, giving small cells which at a temperature of $350^\circ-400^\circ C$ provided 0.16 ampere-hours of service at an average voltage of 1.3 volts.

CONCLUSION

Studies so far made on fused salts by means of conductance and potential measurements have led to some tentative conclusions regarding the nature of the ions in a fused melt and their behavior during electrolysis, and have yielded valuable thermodynamic data on high-temperature reactions. Much more information regarding the structure, the relationship between ions, and the exact mechanism of electrolysis in fused salts is needed, however. The development of some method for the determination of transference numbers would appear to be a necessary step toward such information. After sufficient data from electrochemical studies has been accumulated and correlated with other structural investigations, such as X-ray diffraction studies of fused melts at and above the melting point, for example, it may be possible to describe the mechanism of electrochemical behavior in fused salt systems with more certainty.

BIBLIOGRAPHY

- (1) Lorenz, E., *Electrolyse Geschmolzener Salze*, (1905)
- (2) Mantzell, E., *Z. Elektrochem.* 49, 283 (1945)
- (3) Kraus, C. A., *The Properties of Electrically Conducting Systems*,
Chemical Catalog Co., N.Y. (1932)
- (4) Walden, P., et al., *Z. Physik. Chem.* A131, 1 (1927)
- (5) Walden, P., *ibid* A157 389 (1931)
- (6) Erdey-Gruz, T. Z., *ibid* A178 138 (1937)
- (7) Bloom, H. and Heymann, E., *Proc. Roy. Soc.* A188, 392 (1947)
- (8) Schwarz, K. E., *Z. Elektrochem.* 45, 740 (1939)
- (9) " *ibid* 47, 144 (1941)
- (10) Drossbach, P., *Elektrochemie Geschmolzener Salze*, S. Springer,
Berlin, (1938)
- (11) Drossbach, P., *Trans. Electrochem. Soc.* 70, 249, (1936)
- (12) " *Z. Electrochem.* 43, 891 (1937)
- (13) " *ibid.* 44, 124 (1938)
- (14) " *ibid.* 45, 435 (1939)
- (15) " *Z. Anorg. Chem.* 235, 188 (1938)
- (16) Hildebrand, J.H., and Ruhle, G.C., *J. Am. Chem. Soc.* 49, 722 (1927)
- (17) Salstrom, E. J., and Hildebrand, J. H., *ibid.* 52, 4641 (1930)
- (18) " " *ibid.* 52, 4650 (1930)
- (19) Wachter, A., and Hildebrand, J. H., *ibid.* 52, 4655 (1930)
- (20) Salstrom, E. J., *ibid.* 53, 1794, 3385 (1931)
- (21) " *ibid.* 54, 2653, 4252 (1932)
- (22) Hildebrand, J. H., and Salstrom, E. J., *ibid.* 54, 4257 (1932)
- (23) Salstrom, E. J., *ibid.* 55, 1029, 2426 (1933)
- (24) " *ibid.* 56, 1273 (1934)
- (25) Salstrom, E. J., et al., *ibid.* 58, 1848 (1936)
- (26) Rose, B. A., et al., *Discussions Faraday Soc.* 4, 154 (1948)
- (27) Hamer, W. J., and Schrodt, J. P., *J. Am. Chem. Soc.* 71, 2347 (1949)

SOME PHYSICAL AND CHEMICAL PROPERTIES OF SOLID SUBSTANCES AS A FUNCTION OF SIZE - CHARGE RELATIONSHIPS

Andrew J. Frank

November 1, 1949

Introduction

The transition among a series of related compounds from ionic to covalent bonding and the corresponding change in related properties has been explained by the theory of "ion deformation" or polarization. The ability of the electrical field of one ion to deform the field of another ion has been covered by Fajans (1,2) in the following statements:

- (1) A disproportionate charge on either ion will cause deformation of the other ionic constituent of opposite charge. Since any increase in positive charge over electrical neutrality causes the tightening of electronic orbitals, this effect will be greater on anions than on cations. However, the tendency toward polarization of cations is apparent from a list of the melting points of several anhydrous metal chlorides - Table I - and by the restriction of ionization largely to elements of low valence and to the transitional elements in the lower valence states.
- (2) For a given charge, the smaller the cation the greater is the deformation produced in the anion - the more concentrated the effect of the charge. This is to be noted in the tendency toward ionic character on the part of heavier elements (possessing greater ionic radius) of the same valence type, Table II.
- (3) The larger the anion the more loosely are the outermost electrons held, and the more easily deformed are their orbitals, Table III.
- (4) Ions whose outermost electrons conform to the rare gas structure have less deforming power than those ions (of transition elements) whose electronic configurations consist essentially of 18 outer electrons. For example, the univalent halides of Na, K, Rb, and Cs are ionic in character, even in the gaseous state; the cuprous halides have covalent lattices; and AgCl has been shown to be covalent in the vapor.

Table I.

Melting Points of Anhydrous Metal Chlorides (12)

| <u>Ion</u> | <u>Radius (Å)</u> | <u>M.P. of Anhydrous Cl^-</u> |
|-------------------|-------------------|---|
| Na^+ | 0.95 | 804° C. |
| Ca^{++} | 0.99 | 772° |
| Mg^{++} | 0.65 | 712° |
| Al^{+++} | 0.50 | 194° |

Table II.

Melting Points of Alkaline Earth Chlorides (12)

| <u>Ion</u> | <u>Radius (\AA)</u> | <u>M.P. of Chloride</u> |
|------------------|---|-------------------------|
| Be ⁺⁺ | 0.31 | 405° C. |
| Mg ⁺⁺ | 0.65 | 712° |
| Ca ⁺⁺ | 0.99 | 772° |
| Sr ⁺⁺ | 1.13 | 873° |
| Ba ⁺⁺ | 1.35 | 960° |
| Ra ⁺⁺ | > 1.38 | > 1000° |

Table III.

Melting Points of Anhydrous Calcium Halides (12)

| <u>Halide</u> | <u>Radius (\AA)</u> | <u>M.P. of Anhydrous Ca⁺⁺ Salt</u> |
|-----------------|---|---|
| F ⁻ | 1.36 | 1330° C. |
| Cl ⁻ | 1.81 | 772° |
| Br ⁻ | 1.95 | 730° |
| I ⁻ | 2.16 | 575° |

Symmetry and Asymmetry of Electrical Force Fields

In a series of papers (3-9) W. A. Weyl and his coworkers have developed and extended Fajans' rules to explain certain solid-phase phenomena. Weyl considers the electrical force field about an isolated ion to be symmetrical. In a perfect ionic crystal lattice this symmetrical field is reflected in the uniformity of bond distances and bond strengths throughout the lattice. When factors distort the symmetry of these force fields, certain phenomena occur, or the tendency toward their occurrence is increased.

Effect of a Crystal Surface on Force Field Symmetry (4)

The difference between properties exhibited by a crystalline substance within the body of the crystal and at the surface is generally recognized. Weyl (4) discusses several of these properties by a comparison of the structure of crystals with the structure of glass. In crystalline material the distribution of bond distances and bond strengths is limited and defined by the regularity of the crystal structure, while in glass the random array of ions gives rise to a broad distribution of bond strengths.

At a crystal surface the unsaturation of bonding elements causes an alternate strengthening and weakening of the bonds extending into the body of the crystal. This results in a "broadening of the bond strengths" and the production of surface phenomena similar to those occurring in glass - flow during polishing, sintering below the melting point, and recrystallization. Weyl found that ions capable of producing a polarizing effect or of undergoing polarization had a more profound influence on "broadening of the

Volume 100, Number 1, January 1, 1917

Published by the American Medical Association, 535 North Dearborn Street, Chicago, Ill.

Subscription Price, \$5.00 per Annum in Advance

Single Copies, 15 Cents

Entered as Second-Class Matter, October 3, 1911, Post Office at Chicago, Ill., under No. 100,000

Acceptance for mailing at special rate of postage provided for in Act of October 3, 1917, authorized on July 1, 1918

Postage paid at Chicago, Ill.

Copyright, 1917, by American Medical Association

Printed at the American Medical Association Press, Chicago, Ill.

Published by the American Medical Association, 535 North Dearborn Street, Chicago, Ill.

Subscription Price, \$5.00 per Annum in Advance

Single Copies, 15 Cents

Entered as Second-Class Matter, October 3, 1911, Post Office at Chicago, Ill., under No. 100,000

Acceptance for mailing at special rate of postage provided for in Act of October 3, 1917, authorized on July 1, 1918

Postage paid at Chicago, Ill.

Copyright, 1917, by American Medical Association

Printed at the American Medical Association Press, Chicago, Ill.

Published by the American Medical Association, 535 North Dearborn Street, Chicago, Ill.

Subscription Price, \$5.00 per Annum in Advance

Single Copies, 15 Cents

Entered as Second-Class Matter, October 3, 1911, Post Office at Chicago, Ill., under No. 100,000

Acceptance for mailing at special rate of postage provided for in Act of October 3, 1917, authorized on July 1, 1918

Postage paid at Chicago, Ill.

Copyright, 1917, by American Medical Association

Printed at the American Medical Association Press, Chicago, Ill.

Published by the American Medical Association, 535 North Dearborn Street, Chicago, Ill.

Subscription Price, \$5.00 per Annum in Advance

Single Copies, 15 Cents

Entered as Second-Class Matter, October 3, 1911, Post Office at Chicago, Ill., under No. 100,000

Acceptance for mailing at special rate of postage provided for in Act of October 3, 1917, authorized on July 1, 1918

Postage paid at Chicago, Ill.

Copyright, 1917, by American Medical Association

Printed at the American Medical Association Press, Chicago, Ill.

Published by the American Medical Association, 535 North Dearborn Street, Chicago, Ill.

Subscription Price, \$5.00 per Annum in Advance

bond strength distribution", and that the effect was independent of the relative strengths of adjacent bonds, i.e., whether they were weakened or strengthened.

The polarization of surface ions in crystals is held responsible for initiating phase transformation, surface activity of various glasses, and such electrical properties as surface conductivity and changes in the dielectric constant with particle size.

Transition of Mercuric Iodide (3)

The transition of red HgI_2 into the yellow modification on heating and the reverse process on cooling was considered from three standpoints - surface adsorption, photo-chemical changes, and shear transformation.

Mercuric iodide was considered to possess atomic groups with asymmetrical force fields at surfaces, edges, cracks and corners. "Microscopic examination showed that transformations began with these atomic groups". Surface adsorption of gases was found to affect materially the rate of inversion - hydrogen giving the most rapid rate and oxygen the slowest. The polarizability of the gases are in that same order.

The degree to which the red form could be superheated (under uniform heating conditions) as influenced by various adsorbed ions was studied; the results are tabulated in Table IV. The stabilization of the meta-stable form of HgI_2 is due to the adsorption of strongly polarizable ions or molecules, which tend to extend the force field of the crystal lattice beyond its boundaries, thereby increasing the symmetry of the force field.

Yellow crystals of HgI_2 , obtained from solution on cooling, invert almost instantly if the solvent is benzene, but they remain yellow for ten hours in acetone. Again, the polar solvent causes the symmetry of the crystal to be extended beyond its boundaries, and results in stabilization of a meta-stable structure.

Yellow mercuric iodide, stabilized by imbedding in paraffin, was found to invert more rapidly when exposed to light than when allowed to stand in the dark. Light also catalyzes the decomposition of HgI_2 into mercurous iodide and free iodine.

Mechanical forces and shear stresses were found to speed the inversion, the assumption being that these forces create asymmetrical force fields just as did adsorption of ions. Yellow mercuric iodide, on grinding, reverts immediately at room temperatures to the stable red modification.

Table IV

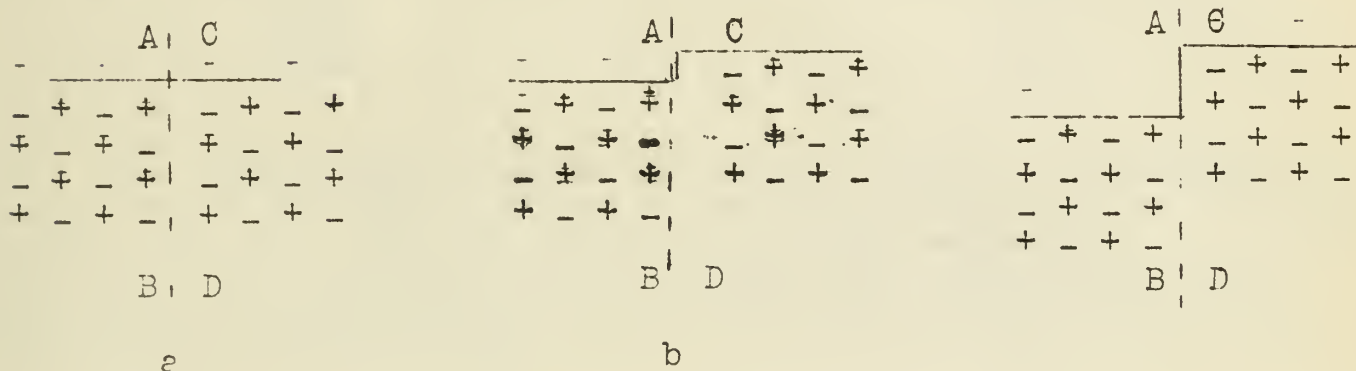
Transition Temperatures of Surface-Charged HgI_2

| <u>Ion Adsorbed</u> | <u>Temp. of Transition</u> |
|---------------------|----------------------------|
| Hg^{+2} | 131-2° C. |
| Pb^{+2} | 131-2° |
| Ba^{+2} | 131-2° |
| Zn^{+2} | 131-2° |
| I^- | 130° |
| Na^+ | 131° |
| Li^+ | 130° |
| Cd^{++} | 129.5° |
| K^+ | 128° |
| — | 126-7° |

red HgI_2 $\xrightleftharpoons[\text{below } 126^\circ]{\text{above } 126^\circ}$ yellow HgI_2

Flow Phenomena in Cubic Crystals (5)

Another property of solids which may be explained qualitatively on the basis of polarization is that of flow under stress.



If shear forces are set up in a crystal such as NaCl , there is no ductility of the crystal, and fracture results. From figured 1, Weyl reasoned that if a crystal is subjected to a shearing stress which would cause plan AB to pass over plane CD, these planes must pass positions where each Na^+ ion as well as each Cl^- ion, is primarily under the influence of an ion of its own kind. The net force acting here is a strong repulsive one causing a separation by fracture of the two planes.

However, AgCl , which has the same crystal structure as NaCl , is quite ductile and can be rolled into sheets. The ductility of AgCl is due to the polarizability of the Ag^+ ion. Thus the approach of one Ag^+ ion to another results in the mutual deformation of the other, and reduces the danger of fracture.

Buerger (10) correlated fundamental ion properties with gliding ease of certain crystals of the NaCl type. The only fundamental property showing regular gradation was that of polarization. Table V show the polarizabilities of several cations and anions, while Table VI shows the combination of these ions and the sum of the polarizabilities of both ions.

THE HISTORY OF THE CITY OF BOSTON

FROM
1630 TO 1800

BY
JOHN H. COLEMAN

AND
EDITED BY
JOHN H. COLEMAN

THE HISTORY OF THE CITY OF BOSTON

FROM
1630 TO 1800
BY
JOHN H. COLEMAN

THE HISTORY OF THE
CITY OF BOSTON
FROM
1630 TO 1800
BY
JOHN H. COLEMAN

THE HISTORY OF THE
CITY OF BOSTON
FROM
1630 TO 1800
BY
JOHN H. COLEMAN

THE HISTORY OF THE
CITY OF BOSTON
FROM
1630 TO 1800
BY
JOHN H. COLEMAN

THE HISTORY OF THE
CITY OF BOSTON
FROM
1630 TO 1800
BY
JOHN H. COLEMAN

Polarizability of Ions

| <u>Cations</u> | | <u>Anions</u> | |
|------------------|-------------------------------------|-------------------|-------------------------------------|
| Pb^{+2} | $3.1 \times 10^{-24} \text{ cm.}^3$ | Te^{-2-} | $9.6 \times 10^{-24} \text{ cm.}^3$ |
| Rb^+ | 1.81 | S^{2-} | 7.25 |
| K^+ | 0.85 | I^- | 6.28 |
| Na^+ | 0.21 | Br^- | 4.17 |
| Mg^{+2} | 0.12 | O^{2-} | 3.1 |
| | | Cl^- | 3.05 |
| | | F^- | 0.99 |

Table VI

| <u>Crystal</u> | <u>Sum of Polarizability of Both Ions</u> |
|----------------|---|
| PbTe | $12.7 \times 10^{-24} \text{ cm.}^3$ |
| PbS | 10.3 |
| KI | 7.13 |
| NaI | 6.49 |
| KBr | 5.02 |
| RbCl | 4.86 |
| NaBr | 4.38 |
| KCl | 3.90 |
| NaCl | 3.26 |
| MgC | 3.2 |
| NaF | 1.20 |

Na^+ - In gliding ease, haloid for haloid, the K^+ salt precedes the Na^+ salt, and for either series the sequence decreases in the order: I^- , Br^- , Cl^- , F^- . The compounds are arranged according to increasing relative ease of gliding on (110) planes and decreasing general plasticity. The ease of gliding on (001) and general plasticity increases from NaF to PbTe.

Photochemistry of Rutile (8)

Rutile, TiO_2 , containing divalent and trivalent transition ions as impurities, shows light absorption out of proportion to the content of the foreign ion. The intense coloration is produced by deformation of the outer orbitals of the low valence ions in an attempt by the crystal to regain electrical neutrality.

In rutile containing ions of valency greater than four, there is evidence of some reduction of the Ti^{+4} to Ti^{+3} to maintain neutrality of the crystal. The bluish-grey crystals cannot be bleached by heating in oxygen, because the crystal does not have oxygen vacancies characteristic of the partially reduced TiO_2 .

Photolytic reactions of TiO_2 are well known and account for the phenomenon of chalking in pigments. In this process TiO_2 liberates atomic oxygen at the crystal surface, which in turn oxidizes the organic material in the binder. That atomic oxygen is released at the crystal surface was shown by the oxidation of 4, 4', 4'' - hexamethyltriaminotriphenyl methane to the corresponding carbinol - crystal violet. No experimental evidence was, however, presented to demonstrate the presence of Ti^{+3} ions under these conditions.

17

18

19

20

21

22

23

24

25

26

27

The similar action of silicates in liberating atomic oxygen has been suggested as a possible cause of silicosis (9). The occurrence of such phenomena is limited by certain conditions, to wit, "the anion must be polarizable and the cation highly polarizing, and the cation must be able to trap permanently the electrons."

A Theory of Detonators (6)

In making a study of detonators, Weyl and coworkers examined the properties of heavy metal chlorates, perchlorates, azides, and fulminates. The anion can be regarded as made up of strongly polarizing central positively charged ion, existing in a symmetrical electrical force field. The introduction of a strongly counter-polarizing cation creates sufficient deformation of the anion so that shear stresses are capable of affecting electron transfers to produce the free elements and the liberation of large amounts of energy.

A study was made of the catalysis of the decomposition of chlorates and perchlorates. The results showed:

- (a) Inert solid substances, containing noble-gas-type ions only, exert a weak effect.
- (b) SnO_2 , TiO_2 (oxides containing non-noble-gas-type ions) are better catalysts.
- (c) Crystalline CoO , CuO , MnO_2 , and PbO_2 were found to be the best catalysts. These compounds form defect lattices, and as such offer strong force fields emanating from their surfaces.

In the chlorates and perchlorates the tendency toward decomposition increases from the K^+ to the Li^+ salt. Among the azides, thermal stability follows the same pattern as among the chlorates and the perchlorates. Some azides, however, decompose violently under shear forces (friction), and "their detonation bears no resemblance to their thermal decomposition".

The alkaline earth azides cannot be brought to explosion by shear forces, while only LiN_3 can be detonated among the alkali azides. Cations of non-noble-gas-type form azides which are readily subject to detonation. Table VII shows several azides and fulminates and their relative stability to shear forces.

Table VII

Comparison Between the Effectiveness of Metal Azides and Fulminates as

| <u>Cation</u> | <u>Detonators</u> | |
|------------------|-------------------|------------------|
| | <u>Azide</u> | <u>Fulminate</u> |
| Cd^{2+} | 1 | 2 |
| Ag^+ | 3 | 4 |
| Pb^{2+} | 5 | - |
| Cu^+ | 6 | 7 |
| Hg^+ | 8 | - |
| Hg^{2+} | - | 9 |

Muraour (11) performed some experiments on picric acid which would tend to support a polarization theory of detonation. Burning Thermit poured into a kettle of fused picric acid resulted only in intense flaming, while pouring a few drops of molten lead into the picric acid produced a violent explosion. Thus the polarization wave was more effective than heat in causing the violent decomposition of the picrate.

Electrical Properties of Glasses (7)

The high dielectric constant of glasses containing PbO or TiO_2 is accounted for by the increased polarizing power of Pb^{+2} and Ti^{+4} ions compared to the alkali metals and alkaline earths usually present in commercial glasses. The latter owe their electron polarization chiefly to the O^{2-} ions.

Anomalous electrical behavior of most commercial glasses is due to three factors:

- (a) Alkali ions are mobile in an otherwise rigid medium.
- (b) A fraction of the alkali ions may change their positions, even at room temperature.
- (c) The interstitial positions in the structure of glasses are not equivalent, but differ slightly in Na-O distances.

Power loss of a glass condenser in an alternating electrical field, and anomalous charge and discharge currents of condensers can be explained as the response of the glass to the above factors.

Critique

The concept developed by Dr. Weyl and his associates in the seven ONR reports considered here has been employed to explain a wide variety of solid-phase phenomena. The experimental evidence cited to support these views was accumulated largely in other laboratories by other investigators, whose objectives were quite different in the interpretation of their data. In several instances, experimental data are completely lacking; it remains to be proved that certain phenomena depend upon polarization effects.

The overall effect of these papers is to create the impression that the authors are attempting to develop an all inclusive, catch-all theory. While asymmetrical force fields may account for many solid-phase reactions, it does not necessarily follow that all phenomena may be explained by such a concept.

Bibliography

- (1) Sidgwick, N.V., "The Electronic Theory of Valency", Oxford University Press, London, 1929.
- (2) Sidgwick, N.V., "The Covalent Link in Chemistry", Cornell University Press, Ithaca, New York, 1933.
- (3) Weyl, W.A., and Enright, D.P., ONR Tech. Report No. 3, Task Order 8, "Influence of Surface Ions on the Rate of Inversion of Mercuric Iodide".
- (4) Weyl, W.A., ONR Tech. Report No. 4, Task Order 8, "On the Surface Structure and Surface Properties of Crystals and Glasses".
- (5) Weyl, W.A., ONR Tech. Report No. 5, Task Order 8, "Discussion of Flow and Rupture of Cupric Crystals from an Atomic Point of View".
- (6) Weyl, W.A., ONR Tech. Report No. 6, Task Order 8, "Decomposition of Complex Anions in Asymmetrical Force Fields".

100

1900

[illegible]

1990

...the ...

- (7) Weyl, W.A., ONR Tech. Report No. 7, Task Order 8, "Dielectric Properties of Glass and Their Structural Interpretation".
- (8) Weyl, W.A., and Forland, T. ONR Tech. Report No. 3, Task Order 11, "Photo-chemistry of Rutile".
- (9) Weyl, W.A., ONR Tech. Report No. 10, Task Order 8, "Active Oxygen Formed at the Surface of Silice and Clay as a Possible Cause of Silicosis".
- {10} Buerger, M.J., The Amer. Mineralogist 15, 226-38 (1930).
- {11} Muraour, H., Trans. Faraday Soc. 34, 985 (1938).
- (12) Chemistry 315, U.I. Lecture Notes, Spring 1948.

COORDINATION OF RARE GASES WITH BORON TRIFLUORIDE

G. L. Eichhorn

November 8, 1949

In an attempt to extend our knowledge concerning the boron trifluoride-rare gas coordination compounds, whose existence was inferred by Booth and Willson (1) from their studies of the argon-boron trifluoride system, Wiberg and Karbe (2) have recently investigated possible compound formation between boron trifluoride and krypton, and xenon, respectively.

The latter workers discovered that, under the conditions of temperature and pressure employed, the rare gas-boron trifluoride mixtures, upon condensation, always form two distinct liquid phases, whose menisci are clearly discernible. Moreover, freezing is observed in each case in the layer of the substance exhibiting the higher freezing point, while the other layer remains liquid at this temperature. The freezing points of the substances decrease from xenon to boron trifluoride to krypton; consequently, in the xenon-boron trifluoride system, the former crystallizes first, whereas in the krypton-boron trifluoride system, the latter is the first to solidify. Both constituents of the mixture are slightly soluble in the liquid phase of the other component, causing, upon cooling, the appearance in both layers of a turbidity, which readily disappears if the temperature is maintained constant. The slight solubility of the two components in each other causes slight freezing point depressions.

Wiberg and Karbe concluded from these observations that no compound formation could be detected in these systems, and subsequently proceeded to reinvestigate the argon-boron trifluoride system. A mixture of argon (f.p. -189°) and boron trifluoride (f.p. -128°) was solidified, and then heated to -135° . The boron trifluoride remained solid, but the argon had liquified and settled to the bottom. Further heating caused the boron trifluoride to liquefy also, and to flow dropwise through the argon layer to the bottom of the tube; at -123° (40 at.) two liquid layers remained. The authors expressed the view that in this system also no compound formation can be demonstrated, and claim that the maxima in Booth and Willson's diagram represent the freezing point of the boron trifluoride phase, and that the eutectic points can be attributed to "secondary effects", such as supercooling and freezing point depression.

It should perhaps be noted that Booth and Willson's accounts of their procedure are much more detailed than those of the German workers.

References:

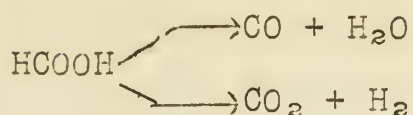
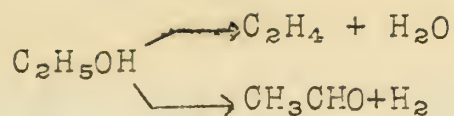
1. Booth and Willson, J. Am. Chem. Soc. 57, 2273-80 (1935).
2. Wiberg and Karbe, Z. anorg. Chem. 256, 307-17 (1948).

SELECTIVE CATALYSIS¹

F. R. Pundseck

:

The simultaneous reactions of dehydration and dehydrogenation in the vapor phase of ethyl alcohol in the one case and formic acid in the other were used to determine and correlate the selectivity of various oxides and salts as catalysts for the reactions. Among the oxides and salts investigated were -ZnO , TiO_2 , Cr_2O_3 , Al_2O_3 ,



CeO_2 , ThO_2 , CaF_2 , $\text{Ca}_3(\text{PO}_4)_2$, and several forms of carbon. These catalysts were prepared in several different forms, generally by the use of heat and recrystallization procedures, in order to determine the effects of preparation upon the selective catalytic properties of the substances.

Experimental data obtained by measuring the flow rate and composition of the decomposition gases made possible the calculation of activation energies and frequency factors for the reactions involved. (Let the velocity of the dehydrogenation reaction be V , then $K = k e^{-\frac{q}{RT}}$ where k = frequency factor, q = activation energy, R = gas constant, T = temperature.)

In the case of ethanol it was found that catalytic dehydration reaction has the higher activation energy. The reverse situation was found to exist in the case of the formic acid decomposition, i.e. the dehydrogenation reaction has the greater activation energy. However, no distinct relation between the activation energy and the chemical nature or physical state of the catalyst was found. Variations in selectivity are evidently due to variations in the frequency factors.

In all the examples studied by the authors it was found that the selectivity is not an intrinsic property of the catalytic substance. In almost all cases it was found that factors which produce sintering or recrystallization of a catalyst, no matter what its chemical nature may be, decrease the dehydrating properties of the catalyst to a greater extent than the dehydrogenating properties. The investigators explained these facts by assuming that dehydrogenation occurs mainly on the flat surfaces of crystalline particles, while dehydration occurs in submicroscopical pores or channels. Thus it would seem logical that certain treatment of these crystals would reduce the small pores to a much greater extent than it decreased the flat surfaces.

Reference:

- 1) Schwab, G. M., and Schwab - Agallidis, E., J. Am. Chem. Soc., 71, 1806 (1949).

THE AQUEOUS CHEMISTRY OF ZIRCONIUM¹

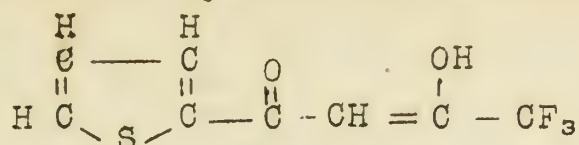
Allen D. Gott

Little conclusive evidence has been obtained concerning the species of zirconium ions present in aqueous solutions of its salts. Several complex ions have been reported but the data could just as well be explained by making other assumptions.

In order to determine the formulas of some of the ions present in aqueous solutions of Zr(IV) salts, a method of liquid-liquid extraction was employed. Because of hydrolysis, it was not possible to use methods such as cell measurements, solubility studies, and freezing point lowering.

McVey and Connick used a chelating agent which forms complexes with Zr(IV) soluble in organic solvents, but which do not form in

aqueous medium. The agent employed was thenoyltrifluoroacetone which can be represented by the enolic formula:



Using benzene as the organic solvent it can be shown that a decrease in chelate concentration in the organic layer is directly related to the concentration of Zr (IV) ion species formed in the aqueous medium. Through mathematical relationship it was possible to measure an extraction coefficient, relate this to ion activities and in turn relate it to ion concentration through the use of equilibrium constants.

It was first necessary to establish the formula of the Zr (IV) chelate formed with thenoyltrifluoroacetone and to prove that no appreciable chelation takes place in the aqueous medium. The latter was proved beyond doubt and the structure of the chelate formed in the organic solvent was shown to be one in which eight oxygens are coordinated to one Zr (IV) ion. Perchloric acid was used to acidify the aqueous medium.

From hydrolysis data it was found that, in 2 M perchloric acid, the average Zr (IV) species has attached to it between zero and one hydroxo group for each Zr (IV) ion.

In studying sulfate complexes it was found that there is an average of one sulfate per Zr (IV) ion at 0.013 M HSO_4^- and an average of two sulfates at 0.3 M HSO_4^- . At both of these points however, a mixture of species was indicated since the successive complexing constants do not differ greatly in magnitude.

Complexing with fluoride ion was found to take place up to 78% in 10^{-5} M HF solutions and all but 0.00012% in 8×10^{-3} M solutions. The average number of fluoro groups per Zr (IV) ion was found to be one at 2×10^{-5} M HF, two at 5×10^{-4} M HF and three at 10^{-2} M HF. Here again all solutions consisted of mixtures.

Chloride and nitrate ions showed similar complexing tendencies. Peroxide complexes also form and are moderately stable. The oxalate complex was found to be very stable but malonate, succinate and glutarate complexes failed to form to any appreciable extent.

Reference:

1. McVey and Connic, J. Am. Chem. Soc. 71, 3182 (1949).

THE CHROMATOGRAPHIC SEPARATION OF PERRHENIC AND MOLYBDIC ACIDS.

J. N. Coker

It has recently been found that certain molybdenum ores contain the element rhenium in amounts approaching one percent (1). These ores thus represent an important source of rhenium.

Several methods previously reported for the separation and concentration of rhenium compounds from molybdenum ores all involve the conversion of the element into perrhenic acid, from which the sparingly soluble potassium salt is separated by the addition of potassium chloride or hydroxide (2).

A new chromatographic procedure for the separation of molybdenum and rhenium has been reported (3), and is based on the fact that from a sulfuric acid solution of molybdic and perrhenic acids, perrhenic acid is more strongly and more rapidly adsorbed on Norite. A consideration of the relative adsorption and desorption rates of

molybdic and perrhenic acids on Norite has indicated that a chromatographic separation of these materials should theoretically be possible. Actually it should be pointed out that, under the conditions of the reaction, perrhenic and molybdic acids cannot be compared rigorously, because the latter acid is present in a polymerized form, the structure of which is not completely known. However, from the reaction rates obtained, it was predicted that the adsorption of perrhenic acid would be favored in the development of a chromatogram.

Treatment of mixtures of molybdic and perrhenic acids with Norite shows that the perrhenic acid is preferentially adsorbed. Using 1.95 N sulfuric acid as both solvent and eluant, rhenium was obtained in yields which were better than 95 per cent of theoretical.

References:

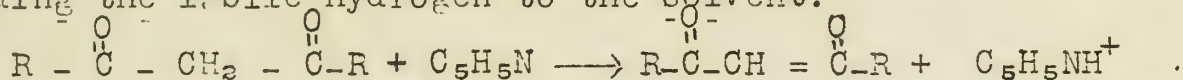
1. Geilmann, Lange, and Barttlingck, Neues Jahrbuch f. Mineralogie, (1948) A 3.
2. Druce, Chemical Products, Vol. XII, No. 9, pp. 326, August (1949).
3. Alexander, J. Am. Chem. Soc. 71, 3943 (1949).

EXAMPLES OF ACID-BASE RELATIONSHIPS IN NON-AQUEOUS SYSTEMS

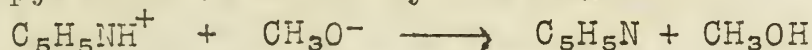
Wm. A. Ziegler

- I. Determination of β -dicarbonyl compounds by titration with sodium methylate. (1,2)

In pyridine solution β -dicarbonyl compounds rapidly enolize, yielding the labile hydrogen to the solvent:



The pyridonium ion can then be titrated with a pyridine solution of sodium methylate, the methylate ion being a much stronger base than pyridine as shown by the reaction:

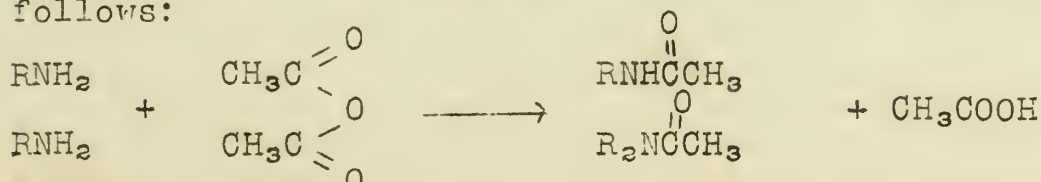


Thus the volume of sodium methylate used is a direct measure of the β -dicarbonyl content of the sample.

Standardization of sodium methylate is made against pure benzoic acid. Thymolphthalein dissolved in pyridine is used as an indicator in both standardization and determination; the color change is from colorless in acid to blue in base.

- II. Determination of tertiary amines in presence of primary and secondary amines. (3,4)

The sample is dissolved in methanol, and excess acetic anhydride is added to react with the primary and secondary amines, as follows:



Tertiary amines, having no free hydrogen, are untouched by the anhydride. Water may even be present since it reacts with excess acetic anhydride to form acetic acid.

[illegible]

In the alcohol medium dissociation of the acetic acid is negligible, and therefore, no reaction with the tertiary amine occurs. Titration of the tertiary amine is then performed with a methanol solution of hydrochloric acid, using methyl orange-xylene cyanole mixed indicator.

References:

- (1) Carbide and Carbon Chemicals Corporation. Works Laboratory Manual, -Works Control Laboratory, S. Charleston, West Virginia, No. 3-1-250, January 6, 1949.
- (2) Ibid., No. 3-1-250.1, January 6, 1949.
- (3) Ibid., No. 3-32-26, June 23, 1947.
- (4) Ibid., No. 3-792-2, February 2, 1948.

HIGHER OXIDES OF THE ACTINIDE ELEMENTS. THE PREPARATION OF Np_3O_8 (1).

Therald Moeller

Recent enunciation of the hypothesis that the heaviest elements are members of an inner transition series (i.e., the actinide series) requires support not only in the preparation and study of similar (often isomorphous) compounds but also in evaluation of the relative stabilities of oxidation states as functions of atomic number. In approaching this problem, the current authors studied the behaviors of oxides and hydrated oxides of protactinium, uranium, neptunium, plutonium, and americium with nitrogen (IV) oxide at temperatures in the range 100-500°. This oxidant was selected because of its reported ability to oxidize lower metal oxides at temperatures ranging from 200° to 400°, since it was realized that because of the increasing thermal instabilities of the higher oxides with increasing nuclear charge oxidations with molecular oxygen at elevated temperatures might be unsuccessful. The procedure amounted to passing nitrogen (IV) oxide, generated by the thermal decomposition of anhydrous lead nitrate, over the oxide at a controlled temperature. Analysis of the product was effected by measurement of oxygen uptake during the reaction and ultimate X-ray examination. Molecular oxygen either accompanying the nitrogen (IV) oxide or resulting from its direct thermal decomposition was shown to be without effect. Evidences were obtained, however, that atomic oxygen produced by the thermal decomposition of adsorbed nitrogen (IV) oxide is the active oxidizing agent.

In the temperature range 250-350°, the oxide U_3O_8 was converted to a brick red UO_3 which differed crystallographically from the yellow UO_3 prepared by the thermal decomposition of uranyl nitrate. Similar treatment of UO_2 gave products ranging from $UO_{2.2}$ to $UO_{2.9}$ with increasing temperature, materials in the range $UO_{2.8-2.9}$ being indistinguishable by x-ray means from UO_3 . These substances may be further examples of the non-stoichiometric compounds which characterize elements in this nuclear charge region. Dried hydrates precipitated from solutions of $Np(IV)$, $Np(V)$, and $Np(VI)$, when oxidized at 300-450°, gave chocolate-brown Np_3O_8 , isomorphous with U_3O_8 but, in apparent violation of the actinide contraction, possessing a slightly larger unit cell than U_3O_8 .

THE UNIVERSITY OF CHICAGO
DIVISION OF THE PHYSICAL SCIENCES
DEPARTMENT OF CHEMISTRY
530 SOUTH EAST ASIAN AVENUE
CHICAGO, ILLINOIS 60607-7070
TEL: 773-936-5000 FAX: 773-936-5001
WWW.CHEM.UCHICAGO.EDU

RECEIVED
JAN 10 1997
FROM: [illegible]
TO: [illegible]
SUBJECT: [illegible]

Dear [illegible]:

[illegible text block containing several paragraphs of text, mostly illegible due to image quality]

Sincerely,
[illegible signature]

This is presumed to be due to looser packing. Thermal decomposition of Np_2O_5 at 700° yielded apple green NpO_2 which underwent no change at 1100° but became highly refractory and insoluble in aqueous acids. Oxides higher than Np_2O_5 were not obtained. Experiments with protactinium (V) oxide were inconclusive, while those with plutonium (IV) and americium (III) oxides at $100-500^\circ$ gave no oxidation beyond the MO_2 step. Further evidence for the decreasing stabilities of higher oxidation states with increasing atomic number is thus presented.

Reference:

- (1) Katz, J.J., and Gruen, D.M.: J. Am. Chem. Soc. 71, 2106 (1949).

THE ACIDS OF THE HYDROGEN FLUORIDE SYSTEM

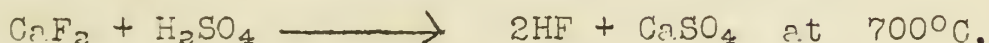
Montfort A. Johnsen

November 22, 1949

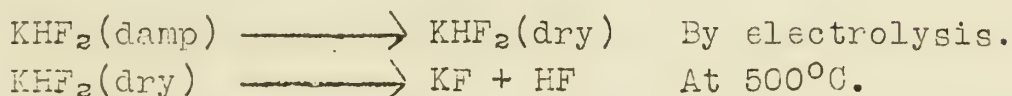
A. INTRODUCTION

I. Preparation of the anhydrous solvent:

a. Industrial Method:



b. Best Laboratory Method:



Unlike synthetic ammonia, commercial anhydrous hydrogen fluoride is usually impure and must be thoroughly dried and processed before it is used as a solvent.

II. Manipulation of the anhydrous solvent:

Solutions of hydrogen fluoride having concentrations greater than 40%, or their vapors, destroy the skin upon contact, forming extremely painful burns which heal slowly. Since physicians are usually unfamiliar with the treatment necessary, persons working in this field should acquaint themselves with first aid measures.

For exacting work, platinum or platinum-gold alloy containers must be used; teflon, stainless steel, copper, or Monel-metal vessels may also be employed. Work should always be carried out within an efficient hood.

III. Physical properties of the anhydrous solvent:

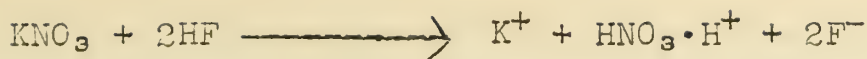
| | HF | H ₂ O | H ₃ N |
|----------------------|-----------|------------------|------------------|
| Boiling Point | 19.54° | 100.00° | -33.35° |
| Melting Point | -83. ° | 0.00° | -77.73° |
| Density at 4° | 0.9918 | 1.0000 | 0.64 |
| Dielectric Constant | 83.6 | 81.7 | 22. |
| Heat of Vaporization | 6030. c/m | 9590. c/m | 5730. c/m |

The anhydrous liquid is colorless and mobile. Electron diffraction has shown that the individual molecules are associated into chain polymers in the gaseous state; Briegleb (1) has indicated that the same type of supermolecule exists in the liquid. Polarization and coulombic attraction, rather than resonance or dipole attractions, are the causes.

IV. Chemical properties of the anhydrous solvent:

Until recently the only known anion in hydrogen fluoride systems was the fluoride ion. Substances capable of furnishing anions to other solvent systems either solvolyzed or were found to be non-ionizing and hence insoluble. For example:



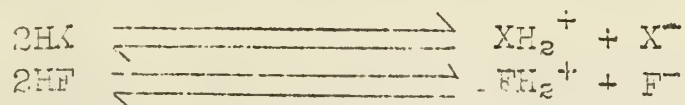


Substances containing the fluoride ion exhibit the same order of solubility in hydrogen fluoride as do the corresponding hydroxides in water. A number of sulfates, perchlorates, and nitrates dissolve but do not ionize. Most halides and oxides are solvolysed.

A large number of cations, however, are possible. The fluorides of the light metals, and of silver (I) and mercury (II) are soluble. On the other hand, few heavy metal salts, such as those of lead, copper, zinc, iron and cobalt, are soluble. Although the cation H_2F^+ exists to the extent that the solvent undergoes selfionization no method for increasing its concentration was known until 1949. Study of acid-base phenomena in anhydrous hydrogen fluoride was, therefore, not possible.

B. ACID-BASE RELATIONSHIPS IN ANHYDROUS HYDROGEN FLUORIDE:

Hydrogen fluoride, like the other two important binary systems, water and ammonia, undergoes auto-ionization according to the general expression:

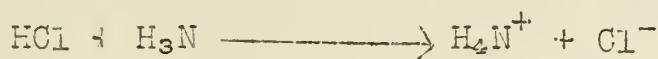


According to the theory of solvent systems (2) any substance capable of increasing the concentration of the cation of a self-ionizing solvent acts as an acid with respect to that solvent. Conversely any substance increasing the solvent anion concentration acts as a base.

Although weak acids and bases can exist in solvents, as cyanide ion in water, the ions derived from the solvent itself represent the strongest acid and base for that solvent system (3). For anhydrous hydrogen fluoride, the strongest possible base is the fluoride anion, while the strongest acid will be the ion H_2F^+ , called the fluoronium ion.

Since it is our purpose to establish acid-base relationships in hydrogen fluoride, it becomes necessary to examine all methods leading to an increase in the concentration of the fluoronium ion. Three classes of substances may be considered:

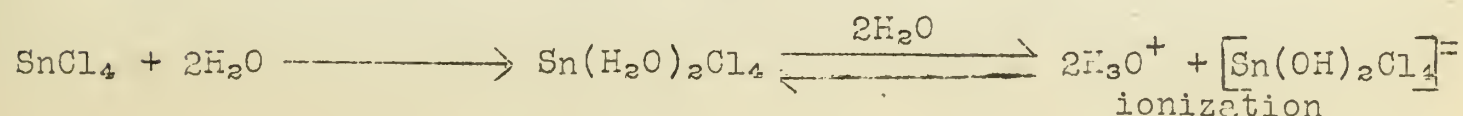
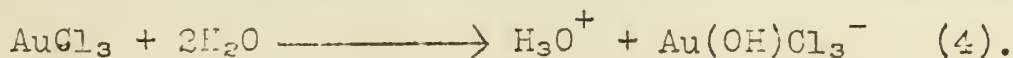
- a. Substances which donate protons to the solvent.



- b. Substances which already contain the solvent cation.

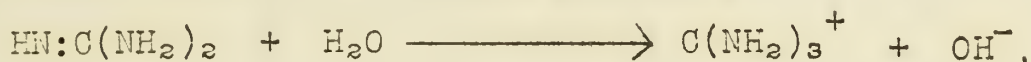


- c. Substances capable of withdrawing the solvent anion.



The degree of self-ionization of the solvents NH_3 , H_2O , and HF increases with increasing difference in electronegativity of the constituent elements. Because of this, the ability of the molecule to produce protons is greatest in hydrogen fluoride; or, it is more capable of acting as acid. It will, therefore, take a stronger protic acid -- on an absolute scale -- to give an acid reaction in liquid hydrogen fluoride than to accomplish the same effect in water.

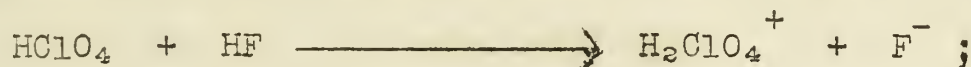
There are probably few, if any, known compounds, capable of donating protons to, and hence acting as acids in, hydrogen fluoride. Most compounds with ionizable protons are derivatives of water or ammonia, having these protons attached to oxygen and nitrogen. Just as ammonia compounds of this type act as bases in water.



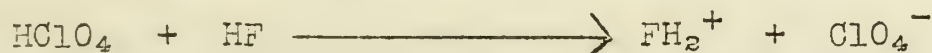
so will most such water system compounds be basic, or at best amphoteric, in hydrogen fluoride,



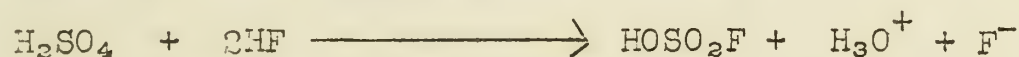
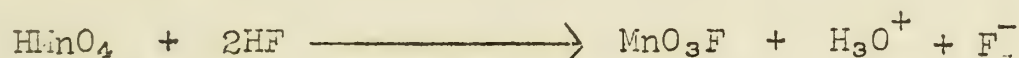
Perchloric acid, perhaps the strongest oxy-acid known (4,5), would appear to act as an amphoteric substance in hydrogen fluoride. Under all normal conditions it seems to behave as a base:



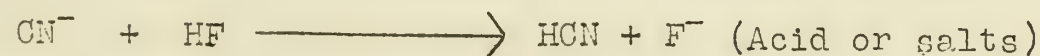
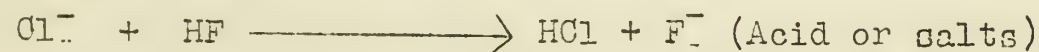
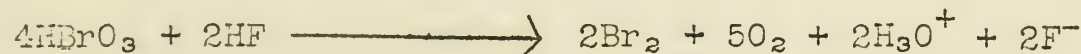
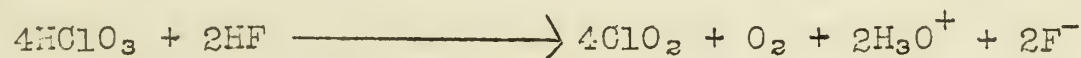
except in strongly basic solution it may act as a weak acid:



Sulfuric and permanganic acids, also very strong acids in the water system, act as bases in hydrogen fluoride, but through a slightly different mechanism:



Still other examples of the solvolysis of acids by hydrogen fluoride are:



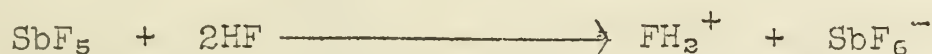
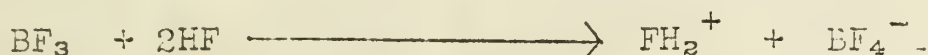
In those cases where the hydronium ion is formed, it must simply be regarded as a salt-forming cation, and thus compared in its role with that of the ammonium ion in water.

Since derivatives of water act as strong acids in water, it would be logical to search for hydrogen fluoride system acids among the derivatives of hydrogen fluoride. The first of these to receive consideration are fluosilicic and fluoboric acids. Upon reflection, however, it is recalled that, although salts and aqueous solutions are known,

these acids do not exist in the free state. This may be explained by the lack of resonance stabilization, steric hindrance, and by the limiting number of stable orbitals available in the case of the pure, and hence unionized, acids. In support of this it can be shown that both these acids are 100% ionized in aqueous solution. The phenomena of reverse normal charge distribution and steric hindrance, are also operative in case of all other possible fluo-acids.

The third and final possibility lies among electron-pair acceptors having a greater attraction for the fluoride ion than has the fluoronium ion. From a somewhat different viewpoint the acid must be able to compete with the fluoride anion for its share of protons. Since fluorine is the most electronegative element, this will constitute a limitation on the number of such substances.

However, there are several additional limiting factors not operating in the water and ammonia systems which impose restrictions. The fact that the valence states of many elements high enough to be acidic would require prohibitive numbers of coordinated fluoride ions to form anions eliminates many more possibilities. The non-availability of sufficient bonding orbitals is a serious limitation for those elements in the second period of the long periodic table, where there are only four orbitals. Examples of the formation of acids by substances surviving these limitations are,



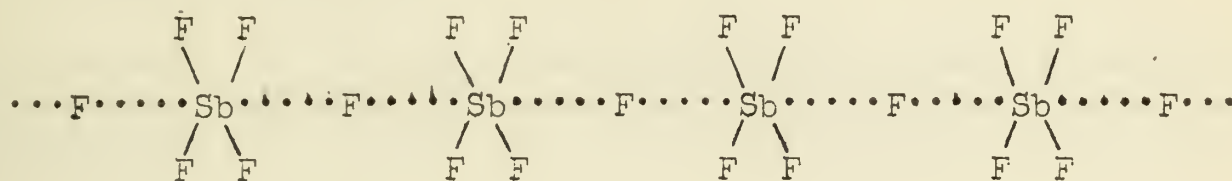
On the basis of these considerations, it is possible to predict with fair certainty which fluorides are capable of forming fluo-acids, as well as the relative strength of these acids.

The ideal fluoracid-forming element will be one just large enough to hold seven or eight fluorine atoms to give an anion of low charge. It cannot be too large, for this will decrease its absolute acidity. The only restriction that cannot be easily determined is whether a given acidic fluoride is capable of adding on still another one or two fluorine ions to give a stable anion. However, there is one rather successful way of forming an opinion about the relative acidity and coordination number. It has been known for some time that the high melting point of aluminum fluoride, compared with that of silicon fluoride is not due to a difference in degree of ionic character (79% and 70%), but to a difference in coordinative degree of unsaturation. Aluminum fluoride, being coordinatively unsaturated, polymerizes; while silicon fluoride has little tendency to do so. Thus the normal melting and boiling points of a compound will be a measure of its ability to form fluoracids.

We will consider now the following four series of compounds, listed along with their boiling points:

| | | | | | | | |
|------------------|------|------------------|------|------------------|------|------------------|-----------------------|
| PF ₅ | -75° | SF ₆ | -64° | SF ₄ | -40° | CF ₄ | -15°C. |
| AsF ₅ | -53° | SeF ₆ | -47° | SeF ₄ | 100° | SiF ₄ | -95° |
| SbF ₅ | 151° | TeF ₆ | -39° | TeF ₄ | ? | GeF ₄ | -104° (6) or -34° (7) |
| | | | | | | SnF ₄ | 705° |

In the first sequence the high boiling point of antimony pentafluoride indicates that it is an associated liquid, hence a strong acid in hydrogen fluoride. None of the compounds in the second series would seem likely candidates. Tellurium (IV) fluoride, and certainly selenium (IV) fluoride would appear to be suitable fluo-acid formers in the third column. In the fourth series two additional factors must be considered: the decreasing ability for the central atom to form double bonds with increasing radius (8), and the ability of stannic fluoride to form a tridimensional space lattice, thus accounting for its exceedingly high boiling point compared with that of antimony pentafluoride which forms only a linear polymer:



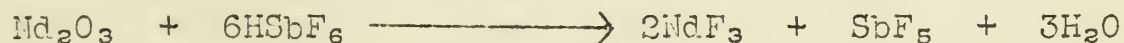
Mention should be made as to methods used to determine acid strength. The following criteria have been used to set up relative acid strengths in anhydrous hydrogen fluoride. Only the strongest acids are capable of dissolving CoF_3 and would be placed in Group I.

- Group I. Ability to dissolve CoF_3 .
- Group II. Ability to dissolve Cr and Mn.
- Group III. Ability to dissolve Mg or to react with CoF_2 and CuF_2 .
- Group IV. Ability to form a salt with AgF (Comparable to NaOH)
- Group V. Very weak --- solution unstable.
- Group VI. Amphoteric substances.
- Group VII. Neutral substances.

EXPERIMENTAL

I. Fluoantimonic Acid (HSbF_6)

Liquid antimony pentafluoride was found to dissolve in hydrogen fluoride with considerable heat of reaction. The solution was found to slowly dissolve the ignited rare earth oxides, giving solutions whose colors (a) depended upon the predominating element and (b) compared closely with those of corresponding aqueous solutions. It is believed that the reactions involve simple neutralization reactions in accordance with the equations:



Addition of sodium fluoride was found to precipitate both tri- and tetravalent rare earth fluorides:

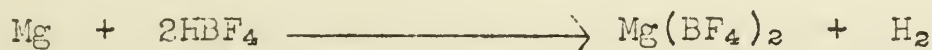


The acid was found to dissolve copper metal forming a yellow solution, presumably of $\text{Cu}(\text{SbF}_6)_2$ and cobalt (III) fluoride, CoF_3 to form a cherry red solution. Upon dilution with hydrogen fluoride however, the $\text{Co}(\text{SbF}_6)_3$ solution suffered solvolysis, indicating that cobalt (III) fluoride behaves as a very weak base in hydrogen fluoride. Fluoroantimonic acid was the only acid found to dissolve cobalt (III) fluoride.

The addition of sodium fluoride to the concentrated solution precipitates NaSbF_6 . It is interesting to note that, the analogous compound, $\text{NaSb}(\text{OH})_6$, is sparingly soluble in water.

II. Fluoboric Acid (HBF_4)

Fluoboric acid solutions were prepared by bubbling boron fluoride into hydrogen fluoride. This solution was observed to attack manganese and magnesium; the reaction is immediately quenched by addition of sodium fluoride.



Most of the fluoborates are insoluble in hydrogen fluoride; the fluorides of silver and copper, which are soluble in HF, react with solutions of HBF_4 to give white and yellow precipitates, respectively. The sodium and potassium salts are soluble.

III. Other Fluo-acids

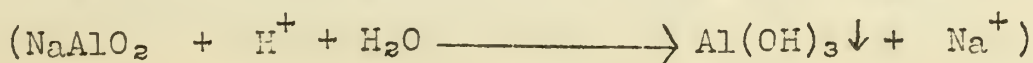
Fluoarsenic acid (HASF_6) was prepared by the action of chlorine tri-fluoride upon a suspension of arsenic in hydrogen fluoride. This solution vigorously attacked magnesium, manganese, mercury, and lead. It failed to dissolve cobalt (II) or copper (II) fluorides, but produced a white precipitate with silver fluoride.

Fluophosphoric (HPF_6) acid was formed by fluorinating red phosphorus suspended in hydrogen fluoride with chlorine trifluoride. The acid was found to have no action on metallic calcium, magnesium or tin, nor on any of the fluorides tested, save silver (I) fluoride, with which it gave a white precipitate. These experimental observations are in accord with the predictions made earlier.

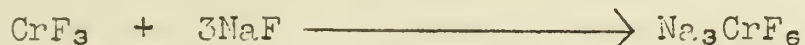
In addition to the above acids, solutions of SeF_4 , TeF_6 , ClF_3 , IF_5 , SiF_4 , GeF_4 , SnF_4 , TiF_4 , VF_5 , CbF_5 , MoF_6 , WF_6 , and ReF_6 were prepared and investigated. It was found, as predicted, that SiF_4 is practically insoluble in hydrogen fluoride, although the gas, when passed through a solution of silver fluoride, AgF , in hydrogen fluoride, precipitated Ag_2SiF_6 . The acidity of solutions of CbF_5 , GeF_4 , TeF_6 , and IF_5 was very low, while that of TiF_4 , SiF_4 , and ClF_3 solutions was almost unrecognizable.

IV. Amphoterism in hydrogen fluoride

Cryolite, Na_3AlF_6 , was found to be quite soluble in hydrogen fluoride; but aluminum fluoride is precipitated upon the addition of boron trifluoride:



Likewise, potassium hexafluorochromate (III) K_3CrF_6 , was found to be soluble in hydrogen fluoride. This compound undergoes solvolysis in HF like that of its hydroxy analog in water, precipitating chromium (III) fluoride. The green precipitate is soluble in an excess of sodium fluoride, giving a green solution:



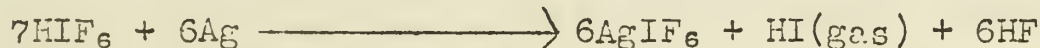
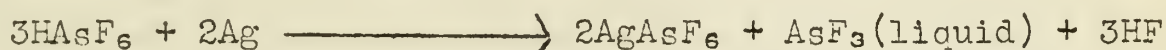
From this solution boron trifluoride reprecipitates the simple fluoride:



These reactions show clearly the amphoteric nature of aluminum and chromium, and prove that the phenomenon of amphoterism can exist in hydrogen fluoride systems as well as in those of water and ammonia.

V. Oxidation - Reduction in HF

It was observed that several fluo-acids are capable of attacking silver and mercury, although they had no effect upon metallic magnesium or calcium. This is explained by the observation that such attack is not accompanied by the liberation of hydrogen, and that acids which fall into this category are capable of being reduced. There re-actions may therefore be similar to those occurring when nitric acid attacks copper. Typical reactions may be represented by the following equations:



Critique: The material presented in the report was abstracted from a dissertation by A. F. Clifford at the University of Delaware, 1949. Although there are several minor points in the Thesis that are open to question, the work has served admirably the major aims of any research program; it has opened up a new field in hydrogen fluoride chemistry; and perhaps more important, has left in its wake a number of unsolved problems that should stimulate further work. In defense of the many conclusions which were drawn from incomplete information, it can only be said that the scope and usefulness of the work would have suffered greatly had this policy not been observed.

BIBLIOGRAPHY

1. Briegleb, Z. physik. Chem., B51, 9, 38, (1941)
2. Cady and Elsey, J. Am. Chem. Soc. 56, 1431, (1934)
3. Hantsch, Z. physik. Chem., 134, 406, (1928)
4. Feigl, "Specific and Special Reactions", Elsevier Publishing Company, Inc. New York, 1940, p. 59
5. Hantsch, Z. physik. Chem., 61, 257, (1908); also ref. 3
6. Ephraim, "Inorganic Chemistry", Interscience Publishers, Inc., New York, 1948, p. 355
7. Booth and Morris, J. Am. Chem. Soc. 58, 90, (1936)
8. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1939, Section 29b.

THE NOMENCLATURE OF ORGANOSILICON COMPOUNDS

Thomas G. Miller

29 November 1949

Although the so-called organosilicon compounds have been the subject of much research over a period of years, the nomenclature of this class of compounds has been neglected. The number of new compounds produced and attending difficulties in indexing made it imperative that a universally accepted system of nomenclature be adopted. The American Chemical Society Committee on Nomenclature recently published an official report on the subject (1), and this year the Committee on Organic Nomenclature of the International Union of Chemistry adopted a definitive set of rules (2).

In order to provide a basis for naming organosilicon compounds as well as to provide an aid in searching the literature, the currently accepted rules will be discussed and compared with older systems encountered in the literature.

Ideally, the pronunciation of the stem sil- should be the same as it is in the element silicon, that is with a short i. The pronunciation, however, is determined by general usage. In general, the i is short in sil- when it is followed by i or a consonant (e.g. silicone, silthiane) and long when followed by a vowel other than i (e.g. siloxane, silane).

Both the ACS and the IUC agree that the term silicone has been adopted by industry and used so generally that it no longer has any significance in chemical nomenclature. Originally intended for the hypothetical compound $\text{H}_2\text{Si}=\text{O}$, it is now generally used as a name for polymeric compounds having the empirical formula $(\text{R}_2\text{SiO})_x$.

Rule 1. Compounds containing only silicon and hydrogen have the generic name silanes and are given a prefix to indicate the number of silicon atoms present. SiH_4 is silane; $\text{H}_3\text{Si}-\text{SiH}_3$ is disilane; $\text{H}_3\text{Si}-\text{SiH}_2-\text{SiH}_3$ is trisilane, etc. The longest chain present serves as the parent compound. Chemical abstracts adopted the ACS committee rules after their publication in 1946. Previous to that, however, no definite system was used. In Chemical Abstracts before 1946 and in many other journals the silanes are found under the heading silicanes (3). The prefix silico- has been used to indicate replacement of carbon by silicon. Thus in Chemical Abstracts, $\text{H}_3\text{Si}-\text{SiH}_3$, disilane, was listed as disilicoethane and also as silicoethane. The prefix per- had also been used to indicate complete replacement of carbon by silicon. In this case disilane would be listed as persilicoethane (4).

Rule 2. Compounds having the formula $\text{H}_3\text{Si}(\text{NHSiH}_2)_n\text{-NHSiH}_3$ are called silazanes with the proper prefix added to indicate the number of silicon atoms present. $\text{H}_3\text{Si}-\text{NH}-\text{SiH}_3$ is disilazane; $\text{H}_3\text{Si}-\text{NH}-\text{SiH}_2-\text{NH}-\text{SiH}_3$ is trisilazane; etc.

These compounds have also been named as amines, imides, and silazines. Stock proposed the name disilylamine for $\text{H}_3\text{Si}-\text{NH}-\text{SiH}_3$ (4). For the same compound Chemical Abstracts used the name silicylimide (3); Sauer proposed the name disilazine (5).

Rule 3. Compounds having the formula $\text{H}_3\text{Si}-(\text{OSiH}_2)_n-\text{OSiH}_3$ are called siloxanes. A prefix indicates the number of silicon atoms present. $\text{H}_3\text{Si}-\text{O}-\text{SiH}_3$ is disiloxane; $\text{H}_3\text{Si}-\text{O}-\text{SiH}_2-\text{O}-\text{SiH}_3$ is trisiloxane; etc.

Other names under which $\text{H}_3\text{Si}-\text{O}-\text{SiH}_3$, for instance, might be found are: silicyl oxide (6), and disilyl ether (5). Kipping named the siloxanes by the number of molecules of water split out during formation and by the number of molecules condensing, e.g. $\text{HOSiH}_2-(\text{OSiH}_2)_4-\text{OSiH}_2\text{OH}$ would be called pentaanhydrohexasilicanediol (5). These compounds are also found under the heading silicone. Stock's system of naming siloxanes was much like the accepted method, differing only in that he used a prefix to denote the number of oxygen atoms in the molecule (4).

Rule 4. (not included in the ACS report). Compounds analogous to the siloxanes, having sulfur instead of oxygen as a connecting element, are called silthianes. The number of silicon atoms present is indicated by a prefix. $\text{H}_3\text{Si}-\text{S}-\text{SiH}_3$ is disilthiane; $\text{H}_3\text{Si}-\text{S}-\text{SiH}_2-\text{S}-\text{SiH}_3$ is trisilthiane; etc.

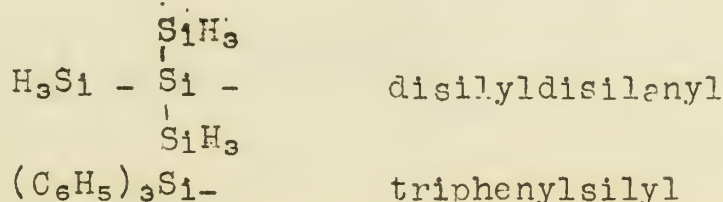
Rule 5. Numbering of compounds occurring under rules 1, 2, 3, 4. Each member of the chain is numbered from one end of the chain to the other. Terminal groups not containing silicon are regarded as substituents. $\text{CH}_3\text{SiH}_2-\text{SiH}(\text{CH}_3)-\text{SiH}_3$ is 1,2-dimethyltrisilane;

$\text{SiH}_3-\text{N}(\text{CH}_3)-\text{SiH}(\text{OCH}_3)-\text{SiH}_3$ is 2-methyl-3-methoxytrilsilazane; etc.

Rule 6. Radical names. Names of radicals are formed in a manner analogous to those of carbon. The following are examples:

| accepted name | | used but not accepted |
|------------------|---|-----------------------|
| silyl | $\text{H}_3\text{Si}-$ | silicyl |
| silylidyne | $\text{H Si}\equiv$ | |
| silylene | $\text{H}_2\text{Si}=$ | silicylene |
| disilanyl | $\text{H}_3\text{Si}-\text{SiH}_2-$ | |
| disilanylene | $-\text{SiH}_2-\text{SiH}_2-$ | |
| trisilanyl | $\text{SiH}_3-\text{SiH}_2-\text{SiH}_2-$ | |
| trisilanylene | $-\text{SiH}_2-\text{SiH}_2-\text{SiH}_2-$ | |
| disiloxanyl | $\text{H}_3\text{Si}-\text{O}-\text{SiH}_2-$ | |
| disilthianyl | $\text{H}_3\text{Si}-\text{S}-\text{SiH}_2-$ | |
| disilthianoxy | $\text{H}_3\text{Si}-\text{S}-\text{SiH}_2\text{O}-$ | |
| siloxyl | $\text{H}_3\text{SiO}-$ | |
| silylthio | $\text{H}_3\text{SiS}-$ | |
| silylamino | $\text{H}_3\text{SiNH}-$ | |
| disilanoxy | $\text{H}_3\text{Si}-\text{SiH}_2\text{O}-$ | |
| disilanylamino | $\text{H}_3\text{Si}-\text{SiH}_2-\text{NH}-$ | |
| disiloxanoxy | $\text{H}_3\text{Si}-\text{O}-\text{SiH}_2\text{O}-$ | |
| disilazanoxy | $\text{H}_3\text{Si}-\text{NH}-\text{SiH}_2\text{O}-$ | |
| disiloxanylamino | $\text{H}_3\text{Si}-\text{O}-\text{SiH}_2\text{NH}-$ | |
| disilazanylamino | $\text{H}_3\text{SiNH}-\text{SiH}_2\text{NH}-$ | |
| cyclohexasilyl | $\text{Si}_6\text{H}_{11}-$ | |

Compound radical names are formed in the usual manner.



3-siloxytrisilthiane $\text{H}_3\text{Si}-\text{S}-\underset{\begin{array}{c} | \\ \text{OSiH}_3 \end{array}}{\text{SiH}}-\text{S}-\text{SiH}_3$

1-siloxy-3-(disilthianoxy)trisilthiane
 $\text{H}_3\text{SiO}-\text{SiH}_2-\underset{\begin{array}{c} | \\ \text{OSiH}_2-\text{S}-\text{SiH}_3 \end{array}}{\text{S}-\text{SiH}}-\text{S}-\text{SiH}_3$

Rule 3. Order of precedence (not included in the ACS report). When there is a choice between two parent names, the order of precedence shall be siloxanes, silthianes, silazanes, and silanes.

| | |
|----------------------------|--|
| 1-(silylthio)disiloxane | $\text{SiH}_3\text{-O-SiH}_2\text{-S-SiH}_3$ |
| 1-(silylamino)disilthiane | $\text{H}_3\text{Si-S-SiH}_2\text{-NH-SiH}_3$ |
| 1-phenyl-3-silyldisiloxane | $\text{H}_3\text{Si-SiH}_2\text{-O-SiH}_2\text{C}_6\text{H}_5$ |

Rule 9. Cyclic silicon compounds of the formula $(\text{SiH}_2)_n$ are called cyclosilanes.

Example: $\text{SiH}_2\text{-SiH}_2\text{-SiHOCH}_3$ Methoxycyclotrisilane

Rule 10. Cyclic silicon compounds of the formula $(\text{SiH}_2\text{O})_n$ are called cyclosiloxanes. The ring is numbered starting with an oxygen atom.

Example: $\text{O}-\text{SiH}_2-\text{O}-\text{SiH}_2-\text{O}-\text{SiH}-\text{OCH}_3$ 2-methoxycyclotrisiloxane

Rule 11. (not in ACS report). Cyclic silicon compounds having the formula $(\text{SiH}_2\text{S})_n$ are called cyclosilthianes. The ring is numbered starting with a sulfur atom.

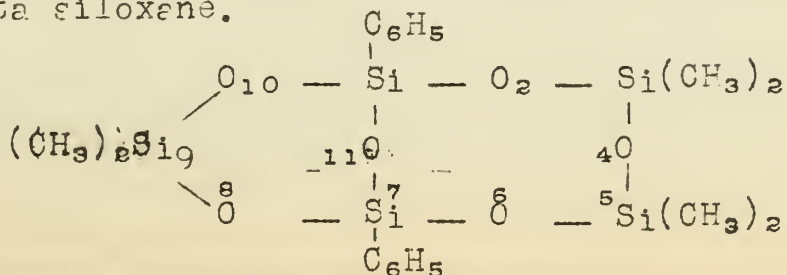
Example: $\text{S}-\text{SiH}_2-\text{S}-\text{SiH}_2-\text{S}-\text{SiH}-\text{OCH}_3$ γ -methoxycyclotrisilthiane

Rule 12. Cyclic silicon compounds having the formula $(\text{SiH}_2\text{NH-})_n$ are called cyclosilazanes. The ring is numbered starting with a nitrogen atom.

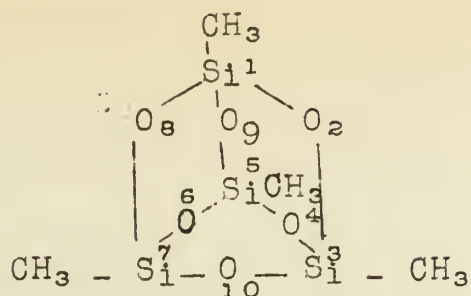
Example: $\text{NH-SiH}_2\text{-NH-SiH}_2\text{-NH-SiH-OCH}_3$ 2-methoxycyclotrisilazane

Rule 13. Polycyclic Siloxanes. Polycyclic siloxanes (polycyclic compounds with only alternating silicon and oxygen atoms) will be named bicyclosiloxanes, tricyclosiloxanes, etc., according to the number of rings present, or as spiro-siloxanes, and will be numbered according to generally accepted methods for carbon compounds of similar nature. Polycyclic silazanes and silthianes are treated similarly.

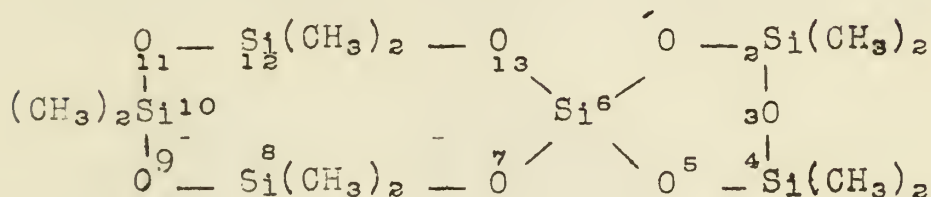
Examples: 3,3,5,5,9,9,-hexamethyl-1,7-diphenylbicyclo (5.3.1) penta siloxane.



tetramethyltricyclo (3.3.1.1^{3,7}) tetrasiloxane



decamethylspiro (5.7) hexasiloxane



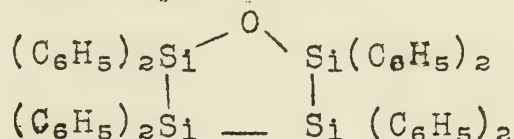
Rule 14. The oxa-aza convention. The names of other compounds containing silicon atoms as hetero members (with or without other hetero members) but not classifiable as linear or cyclic silanes, silazanes, siloxanes, or silthianes are derived from those of the corresponding hydrocarbons with the aid of the oxa-aza convention.

Examples:

2,2,4,4,6,6,-hexamethyl-2,4,6-trisilaheptane
 $(\text{CH}_3)_3\text{-Si-CH}_2\text{-Si}(\text{CH}_3)_2\text{-CH}_2\text{-Si}(\text{CH}_3)_3$

2,4,6,8-tetraoxa-1,3,7,9-tetrāsilanonane
 $\text{H}_3\text{Si-O-SiH}_2\text{-O-CH}_2\text{-O-SiH}_2\text{-O-SiH}_3$

octaphenyl (1-oxa-2,3,4,5-tetrasilacyclopentane)



Sommer and co-workers proposed the generic name silmethylenes for compounds of the general formula $\text{H}_3\text{Si}(\text{CH}_2\text{SiH}_2)_n\text{-CH}_2\text{SiH}_3$ (8). This name was not adopted by the IUC or ACS committee, perhaps because the type of compound is not yet common enough to warrant a class name. Compounds of this type are now named according to the oxa-aza convention described above, which results in cumbersome names when certain units recur in the chain.

In order to shorten the formulas of many large organosilicon compounds, Price (9) and Bluestein (10) have proposed a set of abbreviations for several of the more frequently occurring combinations.

| Radical | abbrev. |
|------------------------------|---------|
| $(\text{CH}_3)_3\text{Si-}$ | M |
| $(\text{CH}_3)_2\text{Si=}$ | D |
| $\text{CH}_3\text{Si}\equiv$ | T |
| Si | Q |

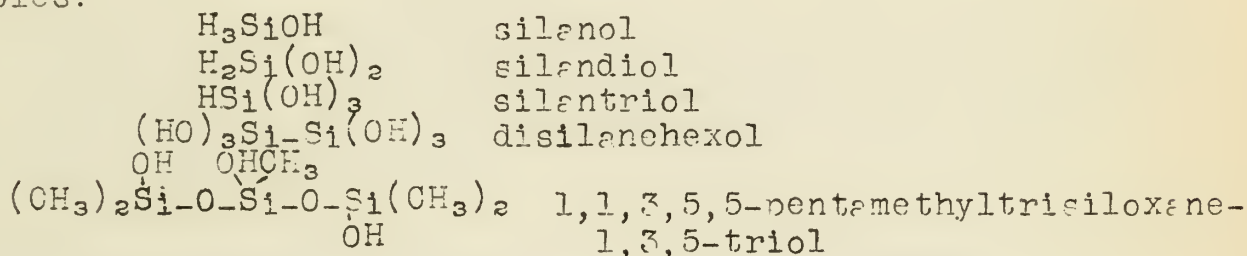
Examples: MODCF₂DOM instead of $(\text{CH}_3)_3\text{Si-O-Si}(\text{CH}_3)_2\text{-CH}_2\text{-Si}(\text{CH}_3)_2\text{-O-Si}(\text{CH}_3)_3$ for the compound 2,2,4,4,6,6,8,8,-octamethyl-3,7-dioxa-2,4,6,8-tetrāsilanonane; and MODCH₂DODCH₂DOM instead of $(\text{CH}_3)_2\text{Si-O-Si}(\text{CH}_3)_2\text{-CH}_2\text{-Si}(\text{CH}_3)_2\text{-OSi}(\text{CH}_3)_2\text{-CH}_2\text{-Si}(\text{CH}_3)_2\text{-O-Si}(\text{CH}_3)_3$ for the compound 2,2,4,4,6,6,8,8,10,10,12,12-decamethyl-3,9-dioxa-2,4,6,8,10-pentasilatridecane.

Ring compounds containing silicon and oxygen in the ring, but not classifiable as siloxanes, are occasionally called oxides (11).

Examples: cyclooctaphenyltetrasilane dioxide $\{C_6H_5\}_8Si_4O_2$
cycloocta-p-tolyltetrasilane oxide $\{C_7H_7\}_8Si_4O$

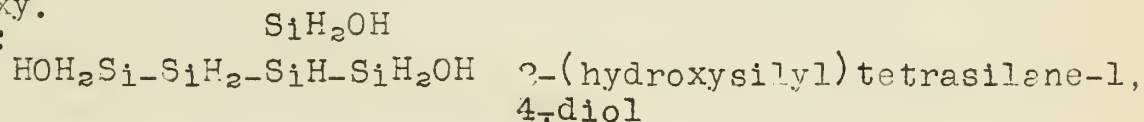
Rule 15. Silanols. Hydroxy derivatives in which OH is attached to silicon are named by adding the suffix -ol, -diol, -triol, etc., to the name of the parent compound. Polyhydroxy compounds in which the hydroxyl group is attached to a silicon atom are named wherever possible in accordance with the principle of treating like things alike.

Examples:



In certain cases, the hydroxy group must be expressed by the prefix hydroxy.

Example:



Various other names have been given to the silanols. Thus the compound diphenylsilanediol, $(C_6H_5)_2Si(OH)_2$, was called diphenylsilicenediol by Kipping and diphenylmonosilanediol by Stock (4). H_3SiOH was listed as silicol in Chemical Abstracts previous to 1946.

Rule 16. Substituents other than hydroxyl groups (functional atoms or groups and hydrocarbon radicals) attached to silicon will be expressed by appropriate prefixes or suffixes, following as closely as possible the accepted rules for organic compounds.

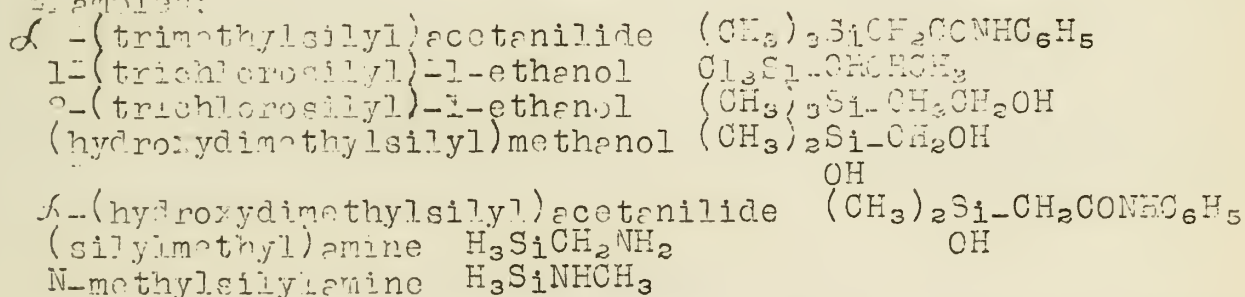
Examples:

| <u>accepted name</u> | <u>formula</u> | <u>other names used</u> |
|-----------------------------|---------------------|---|
| hexachlorodisiloxane | $Cl_3Si-O-SiCl_3$ | hexachlorosilicyl oxide |
| dibutylchlorosilane | $(C_4H_9)_2SiCl_2$ | |
| silylamine | H_3SiNH_2 | |
| silanedi-amine | $H_2Si(NH_2)_2$ | |
| N-methylsilylamine | $H_3SiNHCH_3$ | |
| N,N-dimethylsilylamine | $H_3SiN(CH_3)_2$ | |
| N,N'-dimethylsilanedi-amine | $H_2Si(NHCH_3)_2$ | |
| acetyloxytrimethylsilane | $(CH_3)_3SiOOCCH_3$ | |
| diethoxysilane | $H_2Si(OC_2H_5)_2$ | |
| oxosilane | $H_2Si=O$ | silicone, silicoformaldehyde |
| iminosilane | $H_2Si=NH$ | |
| oxosilan-ol | $H-Si^O-OH$ | silicoformic acid, monosilanic acid |
| oxoethylsilanol | $CH_3CH_2-Si^O-OH$ | ethane siliconic acid, ethyl silicic acid, silicopropionic acid, silicobutyric acid |

Compounds occurring under this rule are named in many different ways throughout the literature. Some of the names are systematic, although not accepted; many are not. Many names are formed by using the prefix *sileo* to indicate that silicon is substituted for carbon, followed by the regular organic or common name, e.g., *sili-*cochloroform for Cl_3SiH , *silico*formic acid for $\text{HSi}(\text{OH})_3$, and *sili-*corrobonic acid for $\text{C}_2\text{H}_5\text{Si}(\text{OH})_2\text{OH}$. In many cases the names of acids are derived in the same manner as the sulfonic acids, e.g., $\text{C}_2\text{H}_5\text{SO}_3\text{H}$ ethane sulfonic acid, $\text{C}_2\text{H}_5\text{Si}(\text{OH})_2\text{OH}$ ethane siliconic acid, $\text{C}_6\text{H}_5\text{Si}(\text{OH})_3$ benzene siliconic acid.

Rule 17. Organo vs. organosilicon nomenclature. Compounds in which there is a carbon atom as well as silicon atom and in which there is a reactive group in the carbon-containing portion of the molecule not shared by a silicon atom are named in terms of the organic parent compound wherever feasible.

Examples:



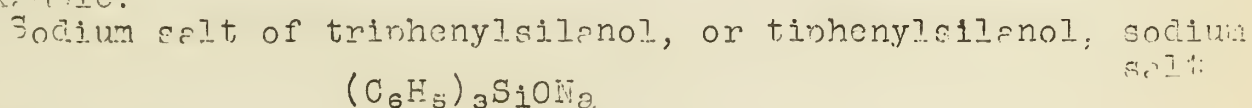
There may be some variation in names occurring under this rule, since a less cumbersome form than the correct one may be used. Thus the ACS committee calls the compound $\text{Cl}_3\text{Si-CH}_2\text{CH}_2\text{OH}$ trichloro (1-hydroxyethyl) silane instead of 1-(trichlorosilyl)-1-ethanol, but calls $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{OH}$ 2-(trimethylsilyl)ethanol, as does the IUC committee. The ACS committee also calls $\text{H}_3\text{SiNHCH}_3$ methylamino-silane, and $\text{H}_2\text{Si}(\text{NHCH}_3)_2$ di(methylamino) silane, c.f. examples above.

Rule 18. Metallosilicon Compounds. Compounds in which metals are combined directly with silicon are, in general, named as derivatives of the metal; as (triphenylsilyl)lithium for $(\text{C}_6\text{H}_5)_3\text{SiLi}$. In exceptional cases, however, the metal may be named as a substituent as, sodium p-sodiosilylbenzoate



Rule 19. Metallic salts. Metallic salts of hydroxy derivatives are named in the customary manner.

Example:



The ACS committee suggested replacing the -ol ending by -olate and placing the name of the metal before. According to this system the compound would be named sodium triphenylsilanolate. The -olate ending was not included in the IUC report.

Perhaps the most serious objection to the now established rules is the lack of correlation in many cases between the name given a compound and its chemical properties. This is especially evident in the case of compounds in which there is an oxosilanol ($R-Si^O-OH$) group. The commonly used name (alkyl or aryl silicic acid) indicates acid properties much better than does the accepted name. The silicic acid terminology is also familiar by analogy with the commonly used names of other acids, i.e., sulfonic acids phosphonic acids, arsenic acids, etc.

In modeling silicon nomenclature after carbon nomenclature the committees have eliminated the need for memorizing a complete new system. It is questionable, however, whether this system of nomenclature can be extended to include similar series of compounds built around germanium, tin or boron. For example, a compound like dimethyltin would be difficult to name by the above rules, while tetramethyltin, or tetramethylstannane, would easily fit in.

While it is desirable to have as few common names for compounds as possible, it would be somewhat more convenient if names were assigned to some of the more common radicals. t-tetrasilanyl- would be more convenient for $(SiH_3)_3Si-$ than disilyldisilanyl-. The names of long chain substituted compounds are also clumsy. This is inevitable if there is no regularly recurring group in the chain, but when a certain group does recur a special name would be much more convenient.

References

1. Official ACS Report, Chem. Eng. News, 24, 1233 (1946).
2. Minutes of the Amsterdam meetings of the International Union of Chemistry Commission on Organic Nomenclature, Part II.
3. C.A., 39, Appendix II, 407-410 (1946).
4. Stock, Ber., 49, 108-11 (1916).
5. Sauer, J. Chem. Education, 21, 303 (1944).
6. Kipping, Proc. Chem. Soc., 28, 343 (1912).
7. Scott, Chem. Rev., 32, 73 (1945).
8. Sommer, et. al., J. Am. Chem. Soc., 69, 980 (1947).
9. Price, J. Am. Chem. Soc., 70, 3069 (1948).
10. Bluestein, J. Am. Chem. Soc., 70, 3069 (1948).
11. Rochow, E.G., "An Introduction to the Chemistry of the Silicones" J. Wiley and Sons, Inc., New York, 1946.

Introduction

In 1912 Sieverts and Bergner,⁷ while investigating the solubility of helium and argon in a number of metals at elevated temperatures, treated crude uranium powder with hydrogen and found that 100g. of the metal absorbed 1.6 mg of hydrogen at 1100°C. No further information was available until 1931, when it was reported that uranium hydride was formed by the reaction of powdered uranium metal with hydrogen at 200 - 225°C.¹

As a result of the inadvertent formation of the compound during the handling of massive uranium metal in a hydrogen atmosphere, a comprehensive investigation of the hydride has been carried out under the auspices of the Atomic Energy Commission. The characterization of the physical and chemical properties has been conducted at Iowa State College.^{8,2,9}

Uranium hydride is a unique compound in that it cannot be classified exactly with the volatile hydrides, the salt-like hydrides, or the interstitial hydrides. It has metallic properties, is non-volatile, and has a high melting point. It is a compound of definite chemical composition and is completely unrelated in structure to any of the three forms of uranium metal.⁴

Preparation

As has been indicated, uranium hydride can be prepared by the direct combination of uranium with molecular hydrogen at elevated temperatures, the reaction rate being a maximum at 230-260°C.⁸ It is reported that 100g. of "cleaned" uranium turnings require only 25-30 min. for complete conversion to the hydride, a massive lump of the same weight requiring 90-120 min.⁸

Uranium hydride can also be produced by the action of steam on uranium at 250°C, uranium (IV) oxide being formed simultaneously. Uranium immersed in an inert solvent (mineral oil) reacts with hydrogen only very slowly at 250°C, while the treatment of lumps of uranium with tetralin (C₁₀H₁₂) or decalin (C₁₀H₁₈) at 210°-270°C. for several days produces 3-10% of the hydride.

A corresponding deuterium compound can be prepared by the reaction of uranium with deuterium at elevated temperatures.

Composition and Structure

That uranium hydride is a true chemical compound has been indicated not only by the integral value of the H:U ratio determined by analysis of the compound, but by X-ray diffraction data as well.

The value of the H:U ratio in hydrides prepared under varying conditions of temperature and pressure was 2.96-2.97.⁸ This was less than three by an amount not ascribable to experimental error. Since hydrogen is found not to react with uranium when the uranium is a component of an intermetallic or other compound, the discrepancy was attributed to impurities in the uranium. Actual analysis showed that 1% of the uranium sample consisted of various uranium compounds which could not combine with hydrogen. Thus the H:U ratio would be 1% less than three, or 2.97, the formula being UH₃.

Samples of the hydride prepared at high hydrogen pressures and others prepared with excess uranium metal were subjected to X-ray analysis. In no case was there any alteration in the d spacings. It was concluded, therefore, that the composition of uranium hydride is definite and that there is no appreciable solubility of hydrogen or uranium in the hydride at ordinary temperatures and pressures.

The X-ray diffraction data indicated the lattice of uranium hydride to be cubic and wholly unrelated to that of any of the three forms of the uranium metal. The lattice constant was found to be 6.631\AA , and the unit cell to contain eight uranium atoms.⁴

The crystal structure proposed by Rundle⁴ to correspond to the observed reflections and absences of reflection on the powder pattern was unusual since it was almost lacking in metal to metal bonds. This suggested that the important bonds were metal-hydrogen bonds and that these bonds were such that the structure possessed metallic properties. The positions of the uranium atoms corresponded to a B-tungsten arrangement with two equivalent atoms (termed type A) at Miller indices of 000 and $1/2\ 1/2\ 1/2$, and six equivalent atoms at $1/40\ 1/2$, $1/2\ 1/40$, $01/2\ 1/4$, $3/4\ 01/2$, $01/2\ 3/4$, $1/2\ 3/40$. The type B atoms formed three perpendicular but non intersecting linear arrays of atoms running parallel to the three cubic axes and spaced at half the cube edge, 3.316\AA . Each of these atoms had two equivalent atoms as nearest neighbors at this distance, forming the shortest metal-metal bond of any strength in the structure. Except for this spacing, the shortest metal-metal distance was too long for metal-metal bonding and too short for hydrogen to fit between metal atoms.⁴ Thus, a hydrogen bridge structure and resonating half-bond from type A to type B atoms were proposed.⁵ This concept was supported by Pauling on the basis of theoretical calculations. However, Rundle recently reported⁶ that these positions do not correspond to neutron diffraction data obtained for the compound. The uranium positions in uranium hydride are permitted in space groups O_h^3 , O^2 , T_d^4 , and, with special parameters, in T_h^1 and T^1 . It was not possible to find hydrogen positions compatible with the neutron data in space groups O_h^3 or O^2 , the hydrogen positions involving at least a three-parameter problem.

Physical and Thermodynamic Properties

Uranium hydride prepared at atmospheric pressure is a very fine, black or brownish-grey, pyrophoric powder. It is brittle and has a high melting point ($> 600^\circ\text{C}$). The electrical conductivity is of the same order of magnitude as that of the powdered uranium metal. The density determined by means of X-ray data is 10.92g/cc ($U-19\text{g/cc}$), the corresponding value for the deuteride being 11.11g/cc . (It is interesting to note that the density of hydrogen alone in the uranium hydride (0.14g/cc) is greater than the density of liquid hydrogen itself ($0.07/\text{cc}$) by a factor of two.) The powder can be compressed at pressures up to 22,600 atmospheres to form blocks with metallic appearance and with densities of 8.7g/cc .

Uranium hydride decomposes on heating in a vacuum, producing finely divided uranium and pure hydrogen, the equilibrium pressure at 357°C being -134 mm . The dissociation pressure of the deuteride is about 1.4 times that of the hydride at all temperatures studied. The heat of formation of the hydride and the deuteride is -30.8 kcal/mole .

Density - composition relationships of uranium - uranium hydride and uranium - uranium deuteride mixtures were found to be linear. Also, the dissociation pressure - composition isotherms prepared from equilibrium data obtained for both the formation and decomposition of the hydride showed a wide plateau region. Both of these relationships support the proposal that uranium hydride is a true chemical compound and eliminate the possibility of two hydrides with different dissociation pressures.

Under atmospheric pressure, the rate of reaction of pure hydrogen with massive uranium is greatest at 230 - 260°C, decreasing at both higher and lower temperatures. The reaction rate can be increased by increasing the hydrogen pressure. Powdered uranium prepared by the decomposition of the hydride reacts rapidly with hydrogen at room temperature, fairly rapidly at dry-ice temperature, but not at all at the temperature of liquid nitrogen. At 357°C, the reaction rate of deuterium with powdered uranium is about one-fourth that of hydrogen, the rate becoming equal at dry ice temperatures.

Chemical Properties

A. Action with Common Reagents

Uranium hydride reacts with water to form uranium (IV) oxide and hydrogen. Dilute hydrochloric, sulfuric, perchloric, and phosphoric acids react very slowly. However, with concentrated sulfuric acid the reaction is very rapid with sulfur dioxide, sulfur, and hydrogen sulfide being formed. Hot concentrated phosphoric acid also reacts rapidly with the hydride to form uranous phosphate; glacial acetic acid with a trace of hydrogen chloride gas reacts to form uranous acetate; and nitric acid reacts to form uranyl nitrate. Uranium hydride is oxidized by 30% hydrogen peroxide with the emission of sparks. No reaction is observed with solutions of sodium hydroxide, potassium hydroxide, ammonium hydroxide, and sodium cyanide.

B. Action with Heavy Metal Salt Solutions

A number of heavy metal salts, particularly silver salts, were found to react with uranium hydride. Silver nitrate in aqueous solution is reduced readily liberating silver and hydrogen and forming uranyl nitrate. Reactions were also observed with silver acetate, silver tartrate, and silver fluoride solutions. Silver perchlorate solutions react particularly rapidly, and it was found that some of the perchlorate ion itself is reduced and precipitated as silver chloride.

A few other heavy metal salts were investigated briefly. Boiling copper sulfate is reduced by uranium hydride to free copper. Mercuric chloride solution causes a rapid reaction yielding mercury and mercurous uranous, and uranyl chlorides. A ferric sulfate solution dissolves the hydride at 100°C as does a solution of cupric ammonium chloride.

C. Reactions with Various Gases and Vapors

It was found possible to prepare a number of tri- and tetravalent uranium compounds conveniently by passing certain gases over uranium hydride up to temperatures of 500°C. The products are finely divided anhydrous materials, a great improvement over the fused masses sometimes obtained by other procedures. The following table will indicate some of these reactions.

| <u>Gas</u> | <u>Temp - °C</u> | <u>Product</u> | <u>Gas</u> | <u>Temp-°C</u> | <u>Product</u> |
|--|------------------|--|------------------|----------------|---|
| HF | 20 - 400 | UF ₄ | H ₂ O | 350 | UO ₂ |
| HCl | 250 - 300 | UCl ₃ | H ₂ S | 400 | US ₂ |
| Cl ₂ (diluted) (with He) | 250 | UCl ₄ | NH ₃ | 250 | U ₂ N ₃ - UN ₂ |
| COCl ₂ | 250 | UCl ₄ (+ C or a) (carbide) | N ₂ | 250 | U ₂ N ₃ - UN ₂ |
| CCl ₄ | 250 | " " " | PH ₃ | 400 | U ₂ P ₃ |
| HBr | 300 | UBr ₃ | CO ₂ | 300 | UO ₂ |
| Br ₂ (with He) | 300 - 350 | UBr ₄ | CH ₄ | 550 | UC |

D. Miscellaneous Reactions

When uranium hydride is covered with solvents such as benzene, toluene, hexane, ether, ethanol, etc. the only visible effect is the evolution of small bubbles (not characterized). The reaction with carbon tetrachloride is explosive, however, and other chlorinated solvents such as chlorobenzene and chloroform react slightly with some evolution of heat but do not cause explosions.

Reductions of organic compounds with uranium hydride were conducted using naphthalene, maleic anhydride, and nitrobenzene. Definite reactions occurred but no reaction products were isolated.

Uranium Hydride Dispersions in Mercury

It was observed that on treating uranium hydride powder with mercury, the entire mass is wetted by the mercury and appears to dissolve. Subsequent evidence indicates that these extraordinary amalgams are not true solutions but suspensions. The preparations are extremely bright and shiny, and those containing 20-50% uranium hydride have a marked tendency to adhere to the glass walls of a vessel. No heat is evolved in their formation, thus indicating each particle retains its structure.

In order to determine whether mercury was unique in its ability to wet uranium hydride, samples of the hydride were treated with other metals and metal alloys. A sodium-potassium alloy appeared to wet the uranium hydride and yielded a material of the same general appearance as the uranium hydride-mercury dispersions. Woods metal was also tested by melting several grams with the hydride. The alloy expanded rapidly, forming a spongy mass. A similar effect was observed when tin was melted with uranium hydride.

Discussion

To return to the original statements that uranium hydride is a definite compound and that it does not fall into the categories of saline hydrides, volatile hydrides, and interstitial hydrides, it may be of interest to correlate some of the data which support these proposals.

It has been pointed out already that the H:U ratio in the hydride is an integral value and that the lattice spacings as determined by X-ray analysis are not altered when the compound is prepared at high hydrogen pressures and with excessive amounts of the metal. Also, the nature of the dissociation pressure-composition isotherm indicates that only one compound is formed. The linear nature of the density-composition relationship in uranium-uranium hydride mixtures shows, as well,

that the system consists of either two phases, uranium-uranium hydride, or is a perfect solid solution. The latter possibility is excluded on the basis of X-ray data and by the failure of hydrogen to transfer from the hydride to the metal at 325°C.

The dissimilarity of the hydride structure to that of uranium and the absence of strong metal-metal bonds in the hydride also are indicative of the fact that the hydride is not a solid solution. The chemical and physical properties, as well, do not correspond rigidly to those of interstitial solutions, while the brittleness and high melting point are in keeping with the properties of valence type compounds. However, the appearance and conductivity of the hydride as well as its being wet by mercury are certainly manifestations of its metallic character.

Suggested Applications of Uranium Hydride

In conclusion, it should be pointed out that besides being a chemical oddity, uranium hydride may be of some laboratory importance. Several uses based upon observed physical and chemical properties have been suggested. The compound may be used as a laboratory source of pure hydrogen or deuterium as well as a source of finely divided uranium, which also results from its decomposition. The slight differences in dissociation pressures and between the hydride and deuteride in rates of reaction of hydrogen and deuterium with uranium have suggested a means for the separation of the isotopes of hydrogen. The reaction of the hydride with a number of gases affords a method of preparation for certain uranium compounds otherwise difficult to prepare in pure anhydrous states. Conversion of uranium alloys to powders by hydride formation permits sieving out intermetallic compounds of the uranium which may be present. Short treatments of metallographic specimens of uranium alloys with hydrogen at 250°C provides an etching technique which improves the clarity of the micro-structure. Imperfections in the castings of uranium ingots may be detected by heating in hydrogen. Uranium hydride has also been suggested for use in reductions of organic compounds and the deuteride for introducing deuterium into organic molecules.

Conclusions

Although the authors have indicated that this investigation was of a survey and exploratory nature, it is apparent that even the material which has been covered is incomplete. An attempt to explain some of the unusual observations would have been of great interest.

To conclude that uranium hydride is not a metallic hydride on the basis of the information available is difficult. Certainly, the most convincing pieces of evidence are the excellent results obtained on determining the composition of the hydride and the X-ray data presented. Perhaps, if investigations of other borderline hydrides yield comparable results, the evidence presented here will be more concrete.

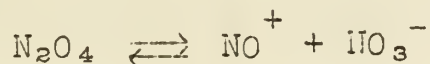
Bibliography

1. F. H. Driggs, Canadian Westinghouse Co., Ltd. U.S. Patents 1,816, 830 and 1,835,024; Canadian Patent 325,501
2. A.S. Newton, et al, Nucleonics 4 (2), 17-25 (1949)
3. L. Pauling and Ewing, J. Am. Chem. Soc. 70, 1660-1 (1948)
4. R. E. Rundle, J. Am. Chem. Soc. 69, 1719 (1947)
5. R. E. Rundle, J. Am. Chem. Soc. 69, 1327 (1947)
6. R. E. Rundle, Abstracts of the 115th Meeting of the American Chemical Society, April, 1949
7. A. Sieverts and E. Bergner, Ber 45, 2583 (1912)
8. F. H. Spedding, et al, Nucleonics 4 (1), 4-15, (1949)
9. J. C. Warf, et al, Nucleonics 4 (3), 43-47, (1949)

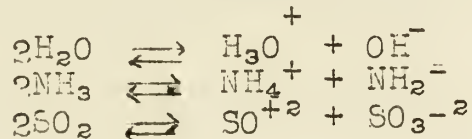
Ralph Gher

December 13, 1949

A solvent system of liquid dinitrogen tetroxide has been postulated by Addison and Thompson¹ which can be compared with the well known water, liquid ammonia, and liquid sulfur dioxide systems. The dissociation of liquid N_2O_4 is assumed to take place according to the following equation:



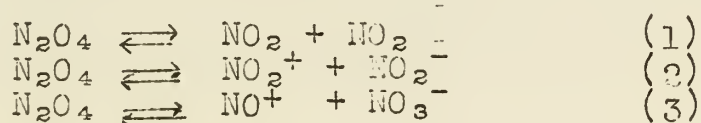
based upon analogy with the self-ionization of water, ammonia and sulfur dioxide:



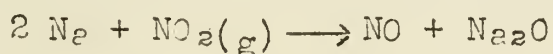
The treatment of the chemistry of N_2O_4 from the point of view of a solvent system has been found to provide a basis for (1) reactions in which liquid N_2O_4 serves as a medium for reaction and (2) reactions in which it serves as a reactant.

Franklin and Farmer² first studied liquid N_2O_4 as a medium for ionic reactions. Although they observed that some organic compounds and non-metallic elements dissolved in the liquid tetroxide, no inorganic salts were soluble. From this fact and the low electrical conductivity (spec. cond. = 2×10^{-8} ohm⁻¹) they concluded that liquid N_2O_4 resembles such organic solvents as benzene. A few reactions of ionic substances have since been reported, however, and these serve as a basis for the work of Addison and Thompson in systematizing the chemistry of N_2O_4 in the liquid state.

In the reactions of liquid N_2O_4 thus far studied the first step has been assumed to be the dissociation of the molecule, characterized by the following possibilities:



Equation (1) represents dissociation occurring at higher temperatures. Since such dissociation occurs only to a limited extent in the liquid state and since mechanisms of gaseous reactions may not be applicable under these conditions this possibility is not considered. For example, Bawn and Evans³ have shown in the flame reaction with sodium that sodium oxide and nitric oxide are formed.



According to Sabatier and Senderens⁴, sodium in liquid N_2O_4 undergoes a reaction forming the nitrate and nitric oxide.



For the reaction to proceed an electron must be transferred from sodium to the nitrosyl ion giving the resonance stabilized nitric oxide molecule. This reaction can best be interpreted on the basis of equation (3).

Levy and Scaife⁵ have shown that dissociation according to equation (2) can occur by preparing aliphatic nitro compounds in liquid dinitrogen tetroxide. N_2O_4 adds to olefinic double bonds giving either nitro-nitro, or nitro-nitrite compounds. They did not actually postulate dissociation of N_2O_4 into $NO_2^+ + NO_2^-$, but concluded that NO_2^+ was responsible for the attack. Ingold⁶ showed that the NO_2^+ ion exists in concentrated sulfuric acid and Bennett considered the nitronium ion the active species in nitration reactions employing nitric and sulfuric acid mixtures. Riessner⁸ has listed a large number of aromatic and aliphatic compounds which give nitro derivatives with N_2O_4 . In these reactions the NO_2^+ group is significant.

Other evidence which seems to indicate dissociation by eqn. (2) has been presented by Exner⁹.



It thus appears that a dissociation represented by equation (2) could be important in purely inorganic reactions and consequently be at variance with the postulate of Addison and Thompson (equation 3). These authors point out, however, that considerable evidence indicates that the mode of dissociation and therefore the nature of the reaction products depends upon whether the reacting substances are covalent or ionic. For example, aniline, and ammonia react explosively with liquid N_2O_4 , yet aniline hydrochloride and the ammonium salts, are not attacked. Only in those cases where a covalent compound is involved does reaction take place. The following general statements seem to be in agreement with the available experimental results.

(a) "In reacting liquid N_2O_4 with covalent compounds dissociation into NO_2^+ and NO_2^- occurs. Since nitrites are not obtained as products in ionic reactions, it is unlikely that NO_2^+ and NO_2^- exist as free ions."

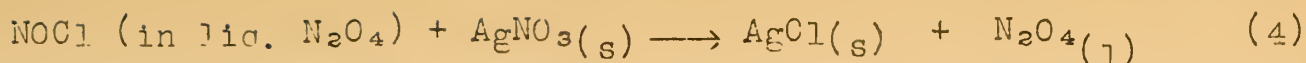
(b) "When liquid N_2O_4 reacts with ionic compounds, dissociation into NO^+ and NO_3^- occurs, and the readiness with which ionic reactions proceed is consistent with the assumption that these ions are present in the tetroxide in small concentrations."

Acid-Base Reactions

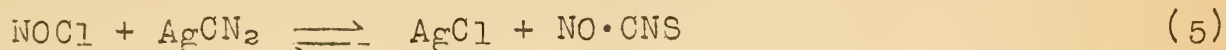
In analogy with the water, ammonia, and sulfur dioxide solvent systems, nitrosyl compounds in which the nitrosyl group functions as a cation are regarded as acids and the nitrates as bases. Neutralization would, therefore, involve reaction between the nitrosyl and nitrate ions ($NO^+ + NO_3^- \longrightarrow N_2O_4$). Since proton transfer is not involved, the Bronsted-Lowry definitions are not applicable, but the Franklin-Kraus, Lewis, and Cady-Elsey¹⁰ acid-base definitions can appropriately be applied.

The investigation of acid-base reactions is restricted by the low solubility of the simple metal nitrates in the liquid tetroxide. As a solvent, liquid N_2O_4 resembles liquid SO_2 more than it resembles water or liquid NH_3 . The corresponding bases of the sulfur dioxide system also possess low solubility. In both systems conductimetric methods are necessary in order to study acid-base reactions.

Of the available acids, nitrosyl chloride ($NOCl$) is perhaps the most stable and is also miscible with liquid N_2O_4 in all proportions. Solutions of $NOCl$ have been found to react with the metal nitrates. The following reaction proceeds to completion,

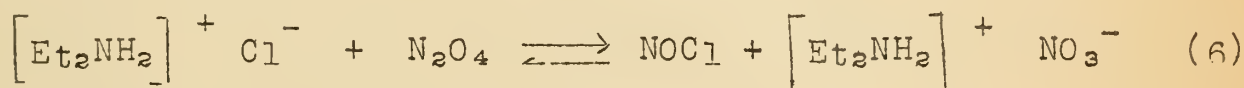


Pure silver chloride and dinitrogen tetroxide undergo no reaction with each other. It should not be implied from the ease with which the reaction takes place that the medium is strongly ionizable with respect to the tetroxide since Perrot¹¹ has shown that the same reaction takes place in the absence of liquid N_2O_4 . Söderbäck¹² found a similar reaction to take place in carbon tetrachloride.



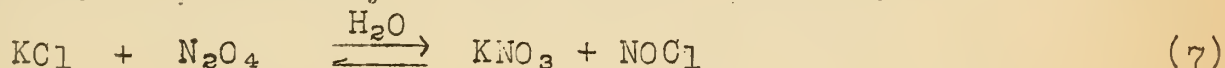
Since NO^+ is involved in reaction (4) and since the tetroxide is a reaction product, this reaction is clearly a neutralization type phenomenon, irrespective of the part N_2O_4 plays in the ionic dissociation of NOCl .

Alkalie metal sulfites and nitrates are known to be insoluble in liquid sulfur dioxide and dinitrogen tetroxide, respectively, although substituted ammonium sulfites and nitrates are readily soluble. (The more extensive replacement of hydrogen atoms by organic radicals, the more soluble is the substituted ammonium salt). For example, diethylammonium nitrate is readily soluble in liquid N_2O_4 . When diethylammonium chloride is added at 0°C the following reaction takes place.

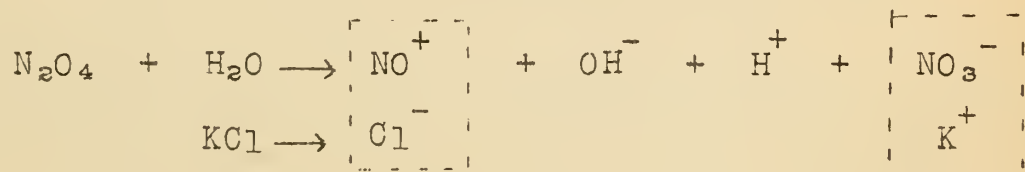


Application is made of this reaction for the preparation of N-nitroso-diethylamine and other nitrosoamines in general¹³.

Whittaker¹⁴ prepared nitrosyl chloride by the following reaction which takes place only if moisture is present.



The water appears to provide the ionizing medium for both N_2O_4 and KCl . Noyes¹⁵ has postulated the mechanism shown below:



From the above reactions (4,5,6,7) it may be concluded that the acid-base reaction $\text{MCl} + \text{N}_2\text{O}_4 \rightleftharpoons \text{MNO}_3 + \text{NOCl}$ (where M is a metal or substituted ammonium ion) is fully reversible in liquid N_2O_4 . When the salts dissolve readily and ionize in the medium, an equilibrium is set up; the forward reaction goes to completion on removal of NOCl . When the salts are insoluble in the medium no forward reaction occurs, but the reverse reaction proceeds to completion.

The Structure of the N_2O_4 Molecule

Several structures for N_2O_4 are presented in literature. Ingold¹⁶ considers structure (I) to be confirmed, based on the olefinic reactions studied by Levy and Scaife⁵ since it is not necessary to assume dissociation other than into $\text{NO}_2^+ + \text{NO}_2^-$. Assuming structure (I) to be correct, dissociation into NO^+ and NO_3^- could occur only by the transfer of an oxygen atom. This is in contradiction to the views of Addison and Thompson that dissociation takes place by electron

...the ... of ...
...the ... of ...
...the ... of ...
...the ... of ...
...the ... of ...



...the ... of ...
...the ... of ...

...the ... of ...
...the ... of ...

...the ... of ...

...the ... of ...
...the ... of ...



...the ... of ...
...the ... of ...
...the ... of ...
...the ... of ...
...the ... of ...

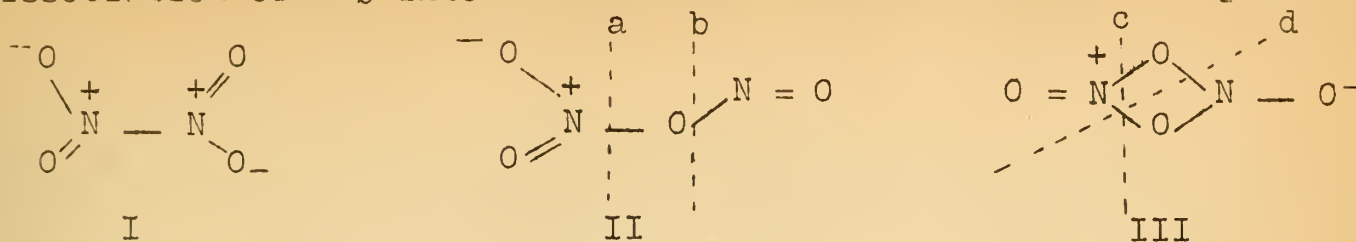
The Synthesis of the ...

...the ... of ...
...the ... of ...
...the ... of ...
...the ... of ...
...the ... of ...

...

...

transfer. In their work with the liquid sulfur dioxide system, Jander and Wickett¹⁷ envisioned the transfer of an oxygen atom in the dissociation of SO_2 into $\text{SO}^{+2} + \text{SO}_3^{-2}$. Structure I is in agreement



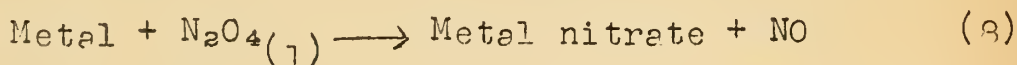
with X-ray data and entropy measurements, however, a structure with similar charges on adjacent atoms is questionable.

Pauling¹⁸ has suggested structure (II) as a more stable configuration. If cleavage of the molecule occurs at (a) dissociation into $\text{NO}_2^{+} + \text{NO}_2^{-}$ would take place; and if cleavage, at (b), dissociation into $\text{NO}^{+} + \text{NO}_3^{-}$ could occur. Thus the two modes of dissociation according to covalent or ionic reactants are satisfied. This structure, however lacks the requirement of symmetry.

Structure (III)¹⁹ appears to be similarly capable of undergoing either type of dissociation without atom transfer. Further, it accounts for vibrational spectra (Raman and Infra red) which call for a planar, highly symmetrical and non-linear structure (20,21).

Liquid Dinitrogen Tetroxide-Metal Reactions

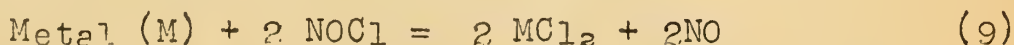
The alkali metals including lithium react readily with N_2O_4 . Magnesium and calcium show very little reaction while some of the transition elements undergo slow reaction. Zinc develops a nitrate coating, mercury reacts to form a mixture of mercuric and mercurous nitrates, and copper a mixture of cupric and cuprous nitrates. The reaction (8) satisfies all reactions studied; in no case was the nitrite formed.



These reactions can be explained by dissociation according to equation (3). Any attempt to explain these reactions by the ionic dissociation: $\text{N}_2\text{O}_4 = \text{NO}_2^{+} + \text{NO}_2^{-}$ would involve the intermediate formation of the nitrite which is stable in the tetroxide.

Nitrosyl Chloride-Metal Reactions

Due to the low concentration of NO^{+} in pure N_2O_4 , reactions in this medium are restricted to the more electropositive metals. If NOCl is added to the tetroxide, the concentration becomes sufficient for reaction to take place with metals normally inert to liquid N_2O_4 . For example, zinc, iron, and tin are attacked by such solutions. These reactions follow the general course shown in (9)



In an analogous manner liquid sulfur dioxide is inert to Na and K, but thionyl chloride (SOCl_2) in SO_2 solutions reacts with these metals, and even with tin and antimony, to give sulfur monoxide as the hypothetical initial product²².



The first part of the paper deals with the general properties of the system. It is shown that the system is stable and that the solution is unique. The second part of the paper deals with the asymptotic behavior of the system. It is shown that the system converges to a steady state and that the convergence is exponential.

In this paper, we consider the system of equations (1) and (2). The first part of the paper deals with the general properties of the system. It is shown that the system is stable and that the solution is unique. The second part of the paper deals with the asymptotic behavior of the system. It is shown that the system converges to a steady state and that the convergence is exponential.

The system of equations (1) and (2) is given by

$$\begin{aligned}
 \dot{x} &= Ax + Bu \\
 y &= Cx + Du
 \end{aligned}$$

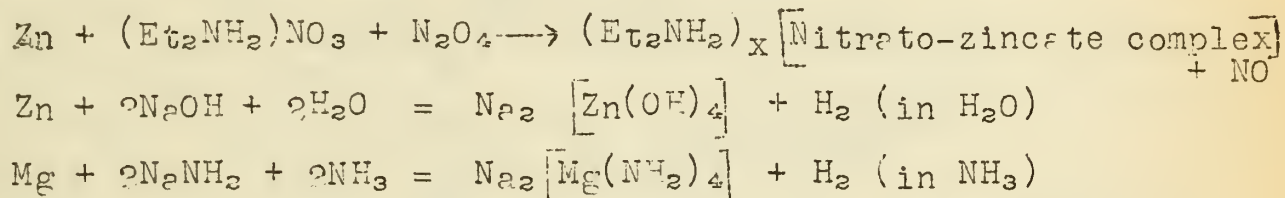
where A , B , C , and D are matrices of appropriate dimensions. The system is said to be stable if the eigenvalues of the matrix A have negative real parts. The system is said to be unique if the solution is unique for any initial conditions and any input u .

In the second part of the paper, we consider the asymptotic behavior of the system. It is shown that the system converges to a steady state and that the convergence is exponential. This is done by analyzing the eigenvalues of the matrix A and showing that they all have negative real parts.

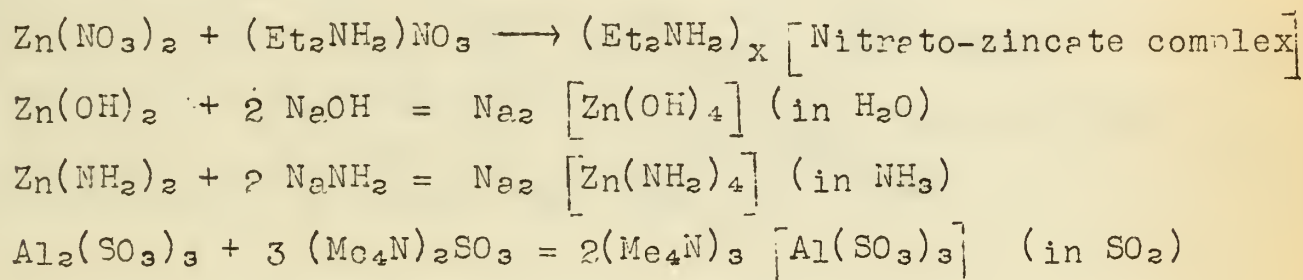
The metal chlorides produced in reaction (9) are usually combined with nitrosyl chloride giving either unstable addition compounds (e.g. $\text{ZnCl}_2 \cdot \text{NOCl}$)²³ or the more stable complex salts of the nitrosyl radical (e.g. $[(\text{NO}^+)_2 (\text{SnCl}_6)^{-2}]$)²⁴ which are acids in this system.

Amphoteric Behavior

Analogy of the tetroxide system to the water, liquid ammonia and liquid sulfur dioxide systems is further extended by amphoteric behavior in liquid tetroxide. For example, zinc reacts slowly with liquid N_2O_4 , but rapidly with NOCl to produce $\text{Zn}(\text{NO}_3)_2$. However, if liquid N_2O_4 is made basic with the addition of diethylammonium nitrate, a vigorous reaction occurs which is similar to comparable reactions in the water and liquid ammonia systems.



The zinc nitrate formed on contact of zinc with liquid N_2O_4 , dissolves when a diethylammonium nitrate solution is added.



Conclusion

Extension of the solvent system concept to liquid N_2O_4 would seem to be justified only in part on the basis of the data thus far presented.

Further studies using inorganic salts of larger cation size may lead to additional information with respect to inorganic reactions in liquid N_2O_4 . For example, in liquid SO_2 , increased cation size enhances the solubility of the sulfites. It might therefore be anticipated that solubilities of inorganic nitrates (base analogs) in N_2O_4 would be greater in the case of the rubidium or cesium salts. These should most certainly be investigated. Addison and Thompson have already shown that greater substitution (hence larger cation size) of the ammonium salts results in an increase in solubility.

Investigations of organic reactions should be restricted because of formation of possible explosive mixtures with N_2O_4 . Nowhere in the article by Addison and Thompson is reference made to possible hazards. Numerous substances such as nitrobenzene, nitronaphthalene, carbon disulfide, aniline, picric acid, and petroleum undergo explosive reaction on contact with N_2O_4 . The explosive power of appropriate mixtures of these substances and liquid N_2O_4 is not only greater than that of most high explosives but such mixtures are also more sensitive to detonation by impact.

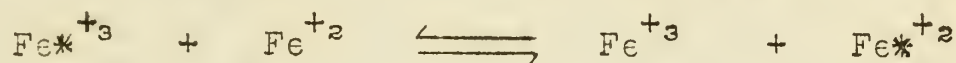
Bibliography

- (1) Addison, C.C. and R. Thompson, J. Chem. Soc., Supple. No. 1., 211, (1949).
- (2) Franklin, P.F., and R.C. Farmer, J. Chem. Soc. 79, 1353 (1901).
- (3) Bawn, C.E.H., and A.G. Evans, Trans. Faraday Soc. 33, 1571 (1937).
- (4) Sabatier, P. and J. B. Senderens, Ann. Chim. Phys. 7, 348 (1896).
- (5) Levy N., and C. Sceife, J. Chem. Soc. 1946, 1093.
- (6) Ingold, C.K., Nature 158, 480 (1946).
- (7) Bennett, G.M., J. Chem. Soc. 1946, 869.
- (8) Riebsomer, J.L., Chem. Rev. 36, 157 (1945).
- (9) Exner, A., J. Chem. Soc. 25, 1072 (1872).
- (10) Cady, H.P. and H. M. Elsey, J. Chem. Ed. 5, 1425 (1928).
- (11) Perrot, R., Compt. rend. 201, 275 (1935).
- (12) Soderbeck, , Ann. 419, 217 (1919).
- (13) Sidgwick, N.V., "The Organic Chemistry of Nitrogen", Oxford Univ. Press, 1937, p. 24.
- (14) Whittaker, C.W., Ind. Eng. Chem. 23, 1410 (1931).
- (15) Noyes, W.A., Ind. Eng. Chem. 24, 1084 (1932).
- (16) Ingold, C.K., Nature, 159, 743 (1947).
- (17) Jander G., and K. Wickert, Z. physikal. chem. 178, 57 (1936).
- (18) Pauling, L., "The Nature of the Chemical Bond", Cornell Univ. Press, 1945, p. 271.
- (19) Longuet-Higgins, H.C., Nature, 153, 408 (1944).
- (20) Sutherland, G.B., Proc. Roy. Soc. A 141, 342 (1933).
- (21) Schaffert, R., J. Chem. Phys. 1, 507 (1933).
- (22) Schenk, P.W., and H. Platz, Z. anorg. chim. 215, 113 (1933).
- (23) Sudborough, , J. Chem. Soc. 59, 655, (1891).
- (24) Asmussen, R.W., Z. anorg. chim. 243, 127 (1939).

ISOTOPIC EXCHANGE BY ELECTRON TRANSFER BETWEEN COMPLEX IONS

IntroductionDescription of an Isotopic Exchange Reaction.

Consider that a solution containing ferric ion is prepared by dissolving FeCl_3 in H_2O , and that a small amount of radioactive iron, in the ferric state, is added to this solution. The resulting solution of ferric iron contains two isotopic species--the one radioactive, the other inactive. Consider next that a solution containing non-radioactive ferrous iron is prepared by dissolving ferrous sulfate in H_2O . Upon mixing these two solutions it is found that, if a sufficient time has elapsed before the ferrous and ferric ions are separated by appropriate means, a certain fraction of the radioactive iron is now present as ferrous iron. This phenomenon is described as an isotopic exchange reaction, and may be represented as follows: (where * is a radioactive species)



The reaction is reversible; by placing the radioactivity initially in the divalent form the presence of the reverse exchange process can be shown to occur.

Classification of Isotopic Exchange Reactions.

The ferrous-ferric exchange is an example of a homogeneous isotopic exchange reaction since the reaction takes place in a single phase. A homogeneous exchange takes place between CO and CO_2 in the gas phase.² If the exchange involves the crossing of a phase boundary the reaction is described as a heterogeneous isotopic reaction.

These reactions may also be classified according to the nature of the exchanging units. These units may be ions with either like or opposite charges; one or both of the units may be neutral molecules.

The mechanism by which the isotopic exchange takes place may also be made a basis for the classification of these reactions. The mechanism may consist of a simple electron transfer, or it may involve the formation of unstable intermediates characteristic of the specific reaction.

Importance of the Study of Isotopic Exchange Reactions.

The study of these reactions is as important to the field of radiochemistry as is the study of ordinary chemical reactions to the fields of inorganic and organic chemistry. Many chemical compounds are quite stable with respect to decomposition or reaction in actuality, but not thermodynamically; in like manner many compounds containing radioactive isotopes are stable with reference to isotopic exchange with other compounds containing the same element. Although the thermodynamic free energy for an exchange reaction is always negative, these reactions are commonly so slow under most conditions that the exchange rates can be neglected; where this is not the case cognizance of the fact must be taken not only for the theoretical interest of exchange but also in order to avoid incorrect conclusions from the use of tracers.

Ferrocyanide - Ferricyanide Exchange

In 1940 Seaborg³ carried out an investigation of the $\text{Fe}(\text{CN})_6^{-3}$ -- $\text{Fe}(\text{CN})_6^{-4}$ system and found no indication of an isotopic exchange of iron between these two ions. This result seemed unlikely in view of the fact that a rapid exchange had been previously reported between (MnO_4^-) and (MnO_4^{2-}) ions. This incongruity prompted W. Burton Lewis at M.I.T. to re-examine Seaborg's data and to revise the methods used by the latter for the separation of the two exchanging ions.⁴ The specific detailed experimental procedures employed in this work follow.

Radioactive Iron Samples.

The radioactive samples were obtained by one of two methods: (a) Bombardment of an iron phosphide target with cyclotron produced 14 mev deuterons - $\text{Fe}^{54}(\text{d}, \text{p})\text{Fe}^{55}$; $\text{Fe}^{58}(\text{d}, \text{p})\text{Fe}^{59}$. The half-lives of the two products are 4 years and 47 days, respectively.⁵ The bombarded target was dissolved in HCl, oxidized with bromine and extracted twice with isopropyl ether from 8M. HCl. The radioactive Fe was detected by the γ radiation from the 47d Fe^{59} in order to eliminate error from the radioactive contaminant extracted by the ether. (b) Slow neutron irradiation of the pure iron metal - $\text{Fe}^{54}(\text{n}, \gamma)\text{Fe}^{55}$; $\text{Fe}^{58}(\text{n}, \gamma)\text{Fe}^{59}$. The product was treated as in (a) above.

Procedures for Initiating and Stopping the Exchange.

The radioactivity was initially concentrated in the ferrocyanide ion. The exchange was initiated by the addition of non-radioactive ferricyanide. In all cases the number of moles of ferricyanide and ferrocyanide in solution were equal. For each such solution another was prepared in which no ferricyanide ions were contained. Three separate chemical methods were employed for the separation of the two exchanging units: (a) Precipitation of $\text{Ag}_4\text{Fe}(\text{CN})_6$; (b) precipitation of $\text{Pb}_2\text{Fe}(\text{CN})_6$ with PbAc_2 ; (c) precipitation of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. For those solutions containing no ferricyanide ion all of the radioactivity resided in the precipitates. The results, based on the radioactivity of the precipitates, are tabulated in Tables I(a), I(b), and I(c). For 100% exchange one-half of the initial radioactivity would be found in the ferricyanide ion.

Table I(a).

Determination of the Per-Cent of Exchange between
Ferrocyanide and Ferricyanide

| Precipitate $[\text{Ag}_4\text{Fe}(\text{CN})_6] + [\text{Ag}_4\text{Fe}^*(\text{CN})_6]$ | Specific Activity (counts/sec./millimole) |
|---|--|
| Solution without $\text{Fe}(\text{CN})_6^{-3}$ | 4.26 |
| Solution with $\text{Fe}(\text{CN})_6^{-3}$ | 1.76 |

$$\% \text{ Exchange} = \frac{(4.26 - 1.76) \times 100}{\frac{1}{2} (4.26)} = \underline{117}$$

Table I(b).

| Precipitation of $\text{Pb}_2 [\text{Fe}(\text{CN})_6] + \text{Pb}_2 [\text{Fe}^*(\text{CN})_6]$ | | | | |
|--|-------------------------|---|-------|------------|
| Species | Time of Exchange (min.) | Specific Activity (ct's/sec./millimole) | | Exchange % |
| | | Initial | Final | |
| $\text{Fe}(\text{CN})_6^{4-}$ | 1 | 35.34 | 18.21 | 99.0 |
| $\text{Fe}(\text{CN})_6^{3-}$ | 1 | 0 | 17.85 | |
| $\text{Fe}(\text{CN})_6^{4-}$ | 31 | 35.12 | 17.96 | 98.6 |
| $\text{Fe}(\text{CN})_6^{3-}$ | 31 | 0 | 17.48 | |

Table I(c).

| Precipitation of $\text{Fe}_4 [\text{Fe}(\text{CN})_6] + \text{Fe}_4 [\text{Fe}^*(\text{CN})_6]$ | | | | |
|--|-------------------------|---|-------|------------|
| Species | Time of Exchange (min.) | Specific Activity (ct's/sec./millimole) | | Exchange % |
| | | Initial | Final | |
| $\text{Fe}(\text{CN})_6^{4-}$ | 30 | 84.7 | 42.3 | 100.8 |
| $\text{Fe}(\text{CN})_6^{3-}$ | 30 | 0 | 43.0 | |

Summary and Conclusion

No matter which of three chemical methods is used for the separation of the exchanging ions, complete exchange takes place in at least ten minutes. It is possible, however, that all three chemical methods catalyze the exchange to approximately the same degree. To eliminate this eventuality it would be more desirable to employ a physical method for the separation process.

Trisethylenediamine Cobalt (II) -- Trisethylenediamine Cobalt (III) Exchange.

While the isotopic exchange of iron between ferricyanide and ferrocyanide proceeds at a rapid rate, it would be expected⁷ that the exchange between two complex ions in which the coordinating agents are non-ionic would be much slower. Experimental studies carried out by W. Burton Lewis⁷ on the isotopic exchange of Co between $[\text{Co}(\text{en})_3]^{+3}$ and $[\text{Co}(\text{en})_3]^{+2}$ confirmed the expected slow exchange rate, making it possible for the first time to undertake a quantitative study of the kinetics and thermodynamics of such phenomena.

Apparatus and Materials for the Exchange.

The tendency for $[\text{Co}(\text{en})_3]\text{Cl}_2$ to absorb oxygen with the formation of a peroxy compound analogous to $[\text{Co}(\text{NH}_3)_5\text{O}]_2\text{Cl}_4$ required the use of an apparatus that would insure the complete absence of O_2 in the system. The tracer was Co^{60} with a half-life of 5.3 years.⁵ In the majority of the exchange experiments the radioactivity was concentrated initially in the divalent complex through the use of a solution containing Co^*Cl_2 .

The inactive tri-valent complex was prepared by the method of Grossman and Schück.⁶

Procedures for the Exchange.

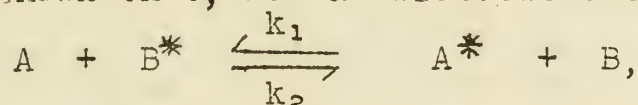
Inactive $[\text{Co}(\text{en})_3] \text{Cl}_3$ and active CoCl_2 were combined in definite concentrations; enough BaCl_2 soln. was added in order to yield a final ionic strength (generally 0.98). After sweeping purified nitrogen through the system the exchange was started by the addition of ethylenediamine. At suitable time intervals aliquots were removed and collected in a small excess of 4N HCl, which stopped exchange instantly, since Co^{++} does not exchange with $[\text{Co}(\text{en})_3]^{+3}$ with a detectable rate at room temperature within at least three months. These two ions were then separated by extraction of the Co^{++} from a 25-30% ammonium thiocyanate solution with 1:1 amyl alcohol, ether mixture and washing the first extract with 30% ammonium thiocyanate. The second extract and the ammonium thiocyanate washing were shaken together to redistribute the cobalt salts to their proper phases.

Properties of the Exchange.

I Kinetic properties.

(a) Rate equation for a generalized isotopic exchange reaction.

It has been shown that, for an isotopic exchange of the form



in which $k_1 = k_2$, the following equation holds:⁷

$$-\ln(1 - \frac{x}{x_\infty}) = \frac{R}{ab} (a+b)t$$

In this equation,

$R =$ a generalized rate function defined $= k(a)^m(b)^n$

$a \equiv [\text{A}^*] + [\text{A}]; b \equiv [\text{B}^*] + [\text{B}]; k = \text{constant}$

(m and n are constants for a given exchange run.)

$x \equiv [\text{A}^*]$ (in terms of measured radioactivity) at time (t)

$y \equiv [\text{B}^*]$ (in terms of measured radioactivity) at time (t)

(x and $y = \text{constant}$ for a given run.)

$x_\infty \equiv [\text{A}^*]$ at $t = \infty$; $y_\infty \equiv [\text{B}^*]$ at $t = \infty$

$\frac{x}{x_\infty} \equiv$ fraction of isotopic exchange at time $= t$

The equality between the rate constants may be assumed for exchanges involving isotopes of elements heavier than oxygen. Thus, for a reversible isotopic exchange reaction a plot of $-\ln(1 - \frac{x}{x_\infty})$ against time should yield

a straight line of slope $\frac{R}{ab} (a+b) = k^*$. This linearity should persist

throughout the course of a given exchange irregardless of the particular values of m and n , the orders of the exchange with respect to (a) and (b), respectively. It is thus possible to obtain values of R from measurements of this experimental slope. Likewise since

$$\ln R = m \ln (a) + n \ln (b) + \ln k,$$

by holding either (a) or (b) constant and varying the other a graph of $\ln R$ against, say, $\ln (a)$ should yield a straight line with a slope equal to m .

(b) Catalytic properties of the exchange.

Oxygen gas exerted a positive catalytic effect upon the rate of exchange between the two complex cobalt ions; this fact was demonstrated by carrying out exchange runs with oxygen present in the system. Glass, silica gel, and nickel metal also catalyzed the exchange. Lusteroid and polystyrene surfaces resemble oxygen in their catalytic effect on the rate; paraffin accelerated the exchange even more than these latter substances.

(c) Dependence of the rate on the pH and en concentration.

The rate was independent of both the ethylenediamine concentration and the pH of the solution (within the range in which $\text{Co}(\text{en})_3^{++}$ exists.) This finding is logical if the reaction is slow on account of the rate of electron transfer only.

(d) Experimental values of k' .

The experimental values for k' were not constant over an entire range of time. Initial values were high after which they decreased to constant values characteristic of the essentially homogeneous reaction. Eventually, k' again increased indefinitely. The early deviations of k' from constancy probably result from the catalytic effect of the minute traces of oxygen remaining in the system. After this oxygen was removed by chemical reaction with the divalent Co complex k' then assumed constant values until seepage of oxygen into the system again destroyed the constancy of the values.

(e) The orders of the exchange.

At 25°C. in a solution of ionic strength 0.98, the orders of the exchange with respect to the total concentration of inactive and active trivalent and divalent complexes were unexpectedly low. (Table II)

Table II
 $\mu = 0.98$; $T = 25^\circ\text{C}$.

| $\text{Co}(\text{en})_3^{++}$ (moles) (liter) | $\text{Co}(\text{en})_3^{+++}$ (moles) (liter) | <u>m</u> | <u>n</u> |
|---|--|----------|----------|
| Variable | 0.0170 | 1.00 | _____ |
| 0.0170 | Variable | _____ | 0.68 |
| Variable | 0.0895 | 0.88 | _____ |
| 0.0895 | Variable | _____ | 0.58 |

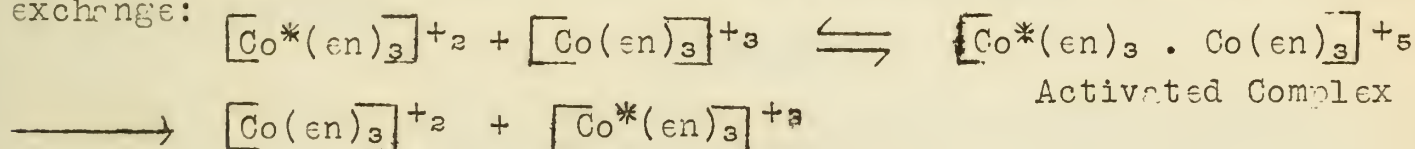
Secondary salt effects, such as polymerization or complex formation, do not satisfactorily explain these values. Polymerization of the trivalent complex would yield either constant values of n for different concentrations of the divalent complex, if the tri-valent complex was completely polymerized, or curves which would be concave downwards (in $R \equiv$ ordinate, against $\ln(b)$), if the polymerization was only slight.

An alternative explanation is that these abnormal exponents have their origin in a salt effect of the primary type - i.e., an effect due to the influence of electrolyte concentrations.

As the fraction of anions in a solution increases in a series of otherwise similar exchange reactions the concentration of such associated ions as $[\text{Co}(\text{en})_3]^{+3}, \text{Cl}^{-+2}$ or $[\text{Co}(\text{en})_3]^{+3}, 2\text{Cl}^{-+1}$ would be increased. Because of the resulting reduced coulombic repulsion forces the exchange could then proceed faster than if the trivalent complex was in the unassociated form. This correlation of the exchange rate with the anion concentration (Cl^{-}) does exist and may be taken as at least partial evidence for the existence of these associated ion pairs or triplets in solution.

II. Thermodynamic properties of the exchange.

The theory of absolute reaction rates, unlike previous theories, states that two reactants must not only possess sufficient energy in order to react but must also form an intermediate activated complex which then decomposes at a specific rate to form the products. Thus, for this exchange:



The rate of exchange will be given by the equation:

$$\frac{dx}{dt} = k_r C_B^* C_A ;$$

$$\begin{array}{l} k_r = \text{specific rate constant} \\ C_B^* = \text{conc. of } [\text{Co}^*(\text{en})_3]^{+2} \\ C_A = \text{conc. of } [\text{Co}(\text{en})_3]^{+3} \end{array}$$

From the above theory,

$$k_r = \left(\frac{kT}{h} \right) K_c ;$$

$$\begin{array}{l} k = \text{Boltzman gas constant} \\ T = \text{temp.}; h = \text{Planck's constant} \\ K_c = \text{equil. const. for formation of} \\ \text{activated complex} \end{array}$$

In combination with standard thermodynamic relations, the following equations can be derived:

$$\begin{array}{l} k_r = \left(\frac{kT}{h} \right) e^{-\Delta F^\ddagger/RT} \\ k_r = \left(\frac{kT}{h} \right) e^{\Delta S^\ddagger/R - \Delta H^\ddagger/RT} \\ k_r = \left(\frac{ekT}{h} \right) e^{-E_{\text{exp}}/RT} e^{\Delta S^\ddagger/R} \end{array}$$

where ΔF^\ddagger , ΔS^\ddagger , and ΔH^\ddagger are the standard free energy of activation, standard entropy of activation, and standard heat of activation, respectively; E_{exp} is the experimental activation energy.

These quantities have been calculated from experimental results and are listed in Table III.

Table III

| $[\text{Co(en)}_3]^{++}$ | $[\text{Co(en)}_3]^{+3}$ | μ | ΔF^\ddagger | ΔH^\ddagger | ΔS^\ddagger |
|--------------------------|--------------------------|----------|---------------------|---------------------|---------------------|
| 0.0895 - - - - - | 0.0170 - - - - - | 0.53 --- | 18,400 --- | ----- | ----- |
| " - - - - - | " - - - - - | 0.98 --- | 18,000 --- | 12,100 | -19.9 |
| " - - - - - | " - - - - - | 1.98 --- | 17,800 --- | 14,500 | -11.1 |
| 0.0170 - - - - - | " - - - - - | 0.98 --- | 18,000 --- | 12,200 | -18.8 |
| " - - - - - | " - - - - - | 1.98 --- | 17,800 --- | 13,700 | -13.7 |
| " - - - - - | 0.0895 - - - - - | " --- | 17,700 --- | 15,000 | -9.1 |
| 0.0895 - - - - - | " - - - - - | " --- | 17,700 --- | 15,100 | ----- |

T = 25°C; energy unit \equiv cal./mole;
 entropy unit \equiv cal./mole/deg.

[] = moles/liter

Conclusion

One of the greatest difficulties inherent in these studies is the inability to insure completely the absence of a heterogeneous catalysis of the exchange; when adequate allowances are made for it's effect the resulting data are of potential value in evaluating not only the kinetic and thermodynamic properties of the exchange (as seen above) but also the structural nature of the exchanging units. Electron transfer exchanges involving the central ion of a complex generally proceed rapidly if the complexing groups are ionic; e.g., $[\text{Fe}(\text{CN})_6]^{-4} \rightleftharpoons [\text{Fe}(\text{CN})_6]^{-3}$, slowly for non-ionic coordination groups; e.g., $[\text{Co}(\text{en})_3]^{+3} \rightleftharpoons [\text{Co}(\text{en})_3]^{+2}$. It would be interesting to investigate the exchange properties for similar electron transfer reactions involving complex ions containing, in their coordination sphere, varying ratio's of both ionic and non-ionic coordinating groups.

BIBLIOGRAPHY

- 1 Ruben, S., Kamen, H. D., Allen, M. B., and Nahinsky, P., J.A.C.S., 64, 2297 (1942)
- 2 Brandner, J. D., and Urey, H. C., J. Chem. Phys., 13, 351 (1945)
- 3 Seaborg, G. T., Chem. Rev., 27, 199 (1940)
- 4 Lewis, W. Burton, ONR Tech. Report #9, M.I.T., January, 1949
- 5 Friedlander, G., and Kennedy, J. W., "Introduction to Radiochemistry", J. Wiley and Sons, New York, 1949
- 6 Grossman, H. and Schück, B., Ber., 39, 1899 (1906)
- 7 Duffield, R. B. and Calvin, M., J.A.C.S., 68, 557 (1946)
- 8 Glasstone, S., Laidler, K. J., and Eyring, H., "Theory of Rate Processes", McGraw-Hill, New York, 1941
- 9 Libby, W. F., J.A.C.S., 62, 1930 (1940)

Sodium-Tungsten Bronzes

J. A. Fuller

January 3, 1950

Introduction

The tungsten bronzes were discovered by Wöhler (1) in 1824 when he reduced acid sodium tungstate with hydrogen. The exact nature of the cubic, bronze-like crystals obtained by Wöhler, and of similar products obtained subsequently, has been the object of innumerable investigations.

Various methods are available for preparing the bronzes. Their composition varies over a wide range and their color, which varies with the composition, is attributed to the presence of tungsten in both the +5 and +6 oxidation states. Chemically, they are inert materials. They are good electrical conductors and have high densities.

Most of the bronzes crystallize in the cubic system but as the composition approaches pure tungstic oxide, lattice contraction in the bronzes results in a change to the tetragonal system. The bronzes are usually represented by the formula Na_xWO_3 , where x has values between 0 and 1.

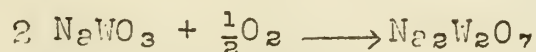
DeJong (2) reported that the yellow sodium bronzes have the perovskite structure. Hägg (3) discovered that the yellow bronzes formed solid solutions with tungstic oxide, accompanied by a change in color.

Straumanis (4) has re-investigated the sodium bronzes in an attempt to determine the lower limit of the cubic bronze series. Straumanis and Dravnieks (5) have investigated the conductivity of the sodium bronzes.

Chemical Properties

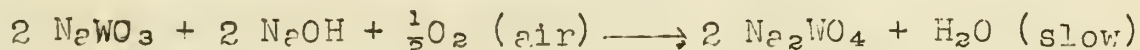
Samples of the purest yellow bronze are shiny, cubic crystals with cleavage parallel to 100. The cleavage planes also have strong metallic luster. These bronzes have a conductivity comparable to graphite ($\sim 400 \text{ ohm}^{-1}/\text{cm}^{-1}$).

Oxygen and Water. - In oxygen free water the luster of the crystals is retained for several months. No solubility was detected in water. In oxygen rich water a slow reaction takes place,



The reaction is accelerated by peroxides.

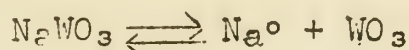
Bases. - Strong bases will dissolve the bronze only if an oxidizing agent is present.



As the percentage of tungstic oxide increases the solubility of the bronze in bases increases.

Acids. - The bronzes are very resistant to attack by acids. This is considered to be due to the formation of surface films containing tungstic acid. This view is supported by the fact that a mixture of HNO_3 and HF is required to dissolve the yellow bronzes.

Thermal Stability. - An equilibrium existing in the crystals is;



An increase in temperature shifts the equilibrium to the right. When a sample of the yellow bronze is heated in air it cakes and turns black. This is caused by oxidation of sodium at the surface and redistribution of tungstic oxide in the lattice to produce a deeper colored bronze. Some of the bronze at the surface is oxidized directly to Na_2WO_7 . Excess tungstic oxide at the surface reacts with Na_2O to form Na_2WO_4 .

If the yellow bronze is heated in a vacuum above 800°C the sodium vapor produced reacts with the bronze to yield tungsten, sodium tungstate and some unidentified material. Some of the sodium vapor is lost by reaction with the glass walls of the reaction tube and the remaining bronze takes on a deeper color.

When a sodium acceptor such as iodine or tungstic oxide is heated with the bronze, the reduction reactions are suppressed. Iodine can extract more than 99% of the sodium. Tungstic oxide however will extract the sodium until a homogeneous composition is attained.

Limit of Solubility of WO_3 in NaWO_3

Samples representative of the sodium bronze series were prepared by dissolving tungstic oxide in the purest yellow bronzes obtainable. The latter were prepared by heating yellow bronzes with sodium or tungsten at $700^\circ\text{--}800^\circ\text{C}$ in an evacuated sealed tube. Several of the yellow bronze samples prepared in this way were shown to have lattice constants exceeding the maximum value obtained by Hagg. The property of lattice shrinkage was used to determine the composition of the samples. Lattice constants were determined by X-ray diffraction (powder method). The stated accuracy in the determination of tungstic oxide was 0.1% by weight.

| <u>Reductant</u> | <u>Lattice Constant - a</u> |
|------------------|-----------------------------|
| Li | 3.8479 |
| Na | 3.8479 |
| W | 3.8494 |
| Na | 3.8502 |
| Na | 3.8504 |
| Na | 3.8504 |
| Na | 3.8508 |
| W | 3.8520 |
| W | 3.8518 |

Figure 1 represents the experimental results. The break in the curve at 27-30% probably indicates a transition but no structural differences could be detected by X-rays. The bronzes in this region probably have the highest conductivity.

THE UNIVERSITY OF CHICAGO
DIVISION OF THE PHYSICAL SCIENCES
DEPARTMENT OF CHEMISTRY

RESEARCH REPORT

ON THE KINETICS OF THE
REACTION OF HYDROGEN
PEROXIDE WITH
SODIUM HYDROGEN SULFATE

BY
J. H. KILPATRICK
AND
J. E. HARRIS

RECEIVED
MAY 15, 1934

Published by the
UNIVERSITY OF CHICAGO PRESS
CHICAGO, ILL.

1934

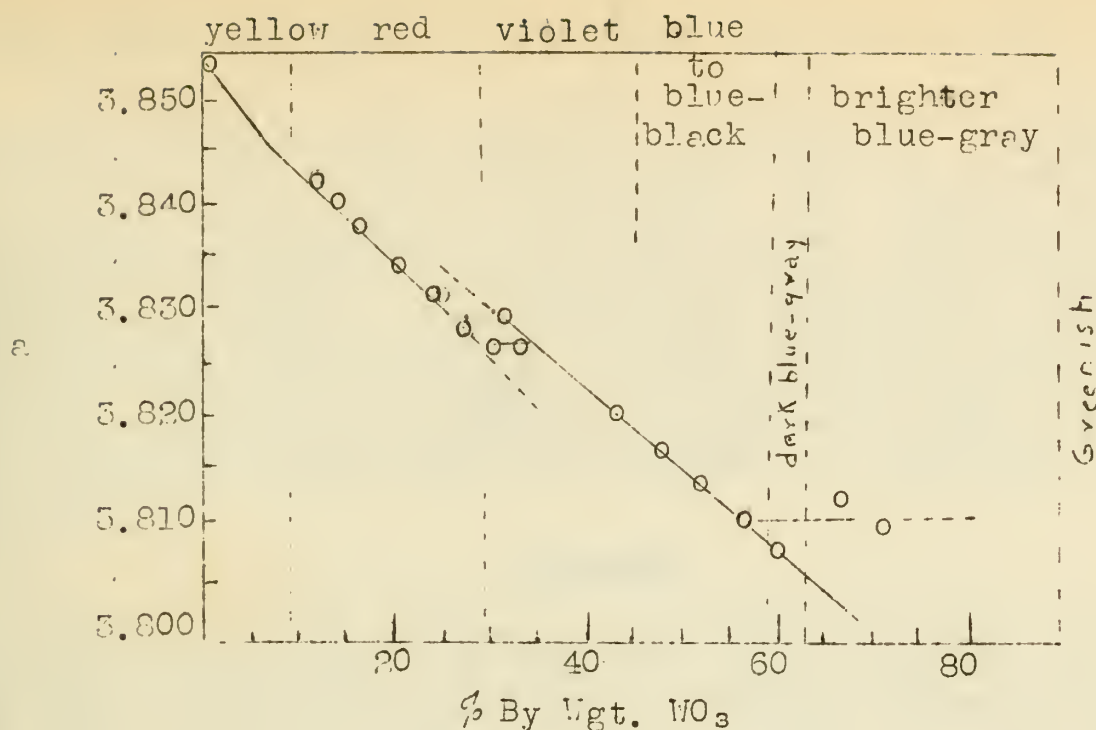


Figure 1

The investigation of the lower end of the curve was carried out utilizing the reactions of the bronzes with tungstic oxide and iodine. In samples prepared with tungstic oxide a transition of the crystal structure occurred between 52% and 57%. With iodine, however, samples were prepared containing up to 81.9% tungstic oxide without destroying the cubic symmetry.

If the bronzes containing - 80% tungstic oxide are subjected to the iodine extraction, samples with blue-green color are obtained. These are of tetragonal structure. Contraction of the tetragonal cell occurs as the sodium content decreases. A sample containing 99.3% tungstic oxide was obtained which had a bright greenish-gray color and which sublimed to form brittle, slightly translucent crystals.

Electrical Conductivity

Hagg observed a large increase in the conductivity of the bronzes with an increase in temperature and suggested progressive scintering as an explanation. A study of the conductivities of the bronzes and of scintered bronzes was made to investigate this possibility.

The resistance of freshly prepared scintered bronze specimens is low but increases rapidly and continuously to high values and the weights increase slightly during an examination in the atmosphere. The resistances do not change in a vacuum or in H_2 , N_2 , H_2S , dry O_2 or pure H_2O vapor. O_2 and H_2O vapor mixtures cause rapid increases in resistance. Recovery of the conductivity may be partially effected by heating or drying over P_2O_5 . Vacuum scintering is necessary for full recovery. The temperature coefficient of conductivity is negative.

The pure bronzes do not show variations in resistance when exposed to moist air. In general the conductivity decreases with increasing tungstic oxide content. Above 50% tungstic oxide large

irregularities are observed. The temperature coefficient of conductivity is negative, indicating electronic conductance.

The behavior of the sintered specimens is believed to be due to formation of Na_2WO_4 and tungsten on sintering. The Na_2WO_4 acts as a binder for the small bronze crystals. Grains of metallic tungsten form conducting bridges in the Na_2WO_4 . The tungsten is apparently activated when embedded in anhydrous Na_2WO_4 and simultaneously adsorbs O_2 and H_2O to form an unstable adsorption compound which disrupts the bridges. The presence of tungsten in sintered samples was proven by X-ray analysis. Various mixtures of yellow bronze, tungsten and anhydrous Na_2WO_4 showed the same behavior as sintered bronzes. Mixtures of tungsten and anhydrous Na_2WO_4 act similarly. When silver is substituted for tungsten, no variation in resistance is observed.

Comment

Apparently the authors accomplished their aims in determining the limit of solubility of tungstic oxide in NaWO_3 and in disproving Hägg's theory of progressive sintering. The description of the tetragonal structures is rather sketchy, however, and a more complete study of this group of substances might prove to be interesting. No explanation is given for the irregularities in conductivities for the bronzes of high tungstic oxide content. This too should be investigated.

Bibliography

- (1) Wöhler, Pogg. Ann. 2, 350 (1824).
- (2) DeJong, Z. Krist. 81, 314 (1932).
DeJong and Stek, *ibid.* 83, 496 (1932).
- (3) Hägg, Z. physik Chem. B29, 192 (1935).
Nature 135, 874 (1935).
- (4) Straumanis, J.A.C.S. 71, 679 (1949).
- (5) Straumanis and Dravnieks, *ibid.* 71, 683 (1949).

Oxidation and Reduction in Geochemistry

Pranlal G. Sheth

January 10, 1949

I. Introduction

The term geochemistry was used for the first time by a Swiss chemist Schonbein in 1838. Early discussions and concepts concerning the science of geochemistry touched the study of mineralogy and geology with special reference to chemical reactions involved therein. To this the concept of thermodynamics - chemical equilibrium - was added by F. W. Clarke² in 1908, while the Russian scientists including Vernadsky and Feroman emphasized the relationship between geochemistry and biological sciences.

A significant contribution towards the development of the science of geochemistry was made by Goldschmidt³ who outlined the main tasks of this border-line field as follows:

1. Determination of the abundance of the elements and of the atomic species of the earth
2. The description of the distribution of the individual elements in the different spheres of the earth and in minerals and rocks
3. The development of the laws governing the abundance and distribution of the elements

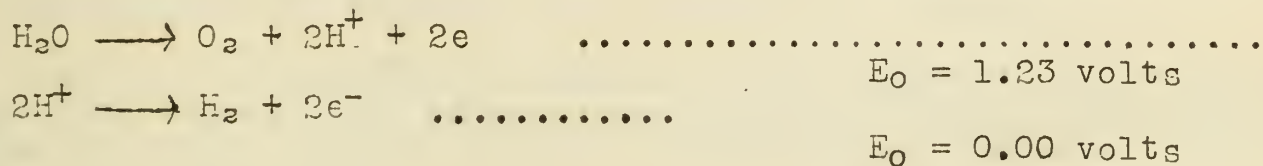
In defining the task of a geochemist Sahama of Finland stated that geochemistry is the study of all that is chemical in geology, and that there should be maintained a chemist's attitude towards the problem under investigation.

An attempt will be made in this discussion to illustrate the effect of oxidation-reduction reactions on the abundance and distribution of elements in our planet.

II. Oxidation-Reduction Reactions in Geochemistry

A. The Range of Oxidation Potentials in aqueous systems in Geochemistry:

Under natural environments this range is limited by the fact that the chemical reactions at or near the earth's surface take place in aqueous solutions. Theoretical limits are:



(It should be noted that negative potential values are assigned to the most active elements i.e., $\text{Zn} \longrightarrow \text{Zn}^{++} + 2\text{e}^-$; $E = -0.76\text{V}.$)

It is within this range that water will decompose, consequently reactions are limited. However, these limits should be corrected for the over-voltage phenomenon, and for the effect of pH, varying generally between 0.00 - 10.0. This correction moves the upper limit to .82 volt and lower limit to -.41 volts. The range here also is 1.23 volts. Consequently, smaller number of reactions are to be expected under the aqueous conditions below the earth's surface.

Redox potentials for marine deposits, lake waters, and soils have been studied by various investigators. Zo Bell⁵ investigated the marine sediments of California coast. He found that sandy to fine grained deposits, rich in organic materials, have oxidation potentials varying from .35 volt to -.50 volt. The pH value was noted to vary from 6.4 to 9.5. Allgeier, Hafferd and Juday⁶ noted that the Wisconsin lake waters had oxidation potential of .38 to .50 volt, the bottom water had potential of -.057 to .44 volt, and the bottom deposits had potential of -.14 to .20 volt. An instrument was developed to determine oxidation potentials of lake waters in situ. Presence of dissolved oxygen, ferrous iron, hydrogen sulphide and organic materials was found to affect the oxidation potential values.

B. Application of Oxidation Potential to Geochemical Problems:

The principle of oxidation potential is capable of wide application in geochemistry to explain the solution, transportation and deposition of those elements which may occur in two or more oxidation states. These applications are discussed particularly by Goldschmidt⁷ and by Chapman and Schweitzer⁸.

C. Occurrence of Native Metals:

The more positive the potential required to remove the electrons from a metal and convert it into a metallic ion, the greater is the tendency for the metal to be found in the native state. On the other hand, if the element has an oxidation potential more negative than that of the hydrogen electrode it is theoretically impossible for it to be discharged from its ions in an aqueous solutions, so that it can possibly only be formed in a nonaqueous environment.

Au and Pt having oxidation potentials more positive than 1.0 volt are found in native state; Cu, Hg, Ag, having oxidation potentials between 0.0 and 1.0 volt are found both in native and combined states. Metals with negative potentials are rarely found in native state. Although lead has a negative value, it is found in native state. Under alkaline or slightly acidic conditions, the $\text{Pb} \longrightarrow \text{Pb}^{++} + 2e$ couple has a potential more positive than 1.

Alkali and alkaline earth metals, Al, Ti, Cr, Mn, etc. are not known in native state because of their highly negative potential values.

D. Conditions for Formation and Stability of Minerals:

Mineral paragenesis is helpful in the study of several geological phenomena. Such study makes it possible to determine the mutual relations and time sequence of mineral deposition as revealed in their association in nature.

For example, when Pb is found associated with $\text{Mn}(\text{OH})_2$ deposition is the result of low temperature geological phenomena. It can be shown that the oxidation potential of the medium must have been negative at the time of its formation and that deposition probably took place in alkaline or weakly acidic medium. Alkaline nature is confirmed by the occurrence of the mineral $\text{Mn}(\text{OH})_2$, pyrochroite. High positive potentials are required to convert divalent cobalt and lead into trivalent cobalt and lead dioxide in acid solution; the presence of stainierite CoOOH , and of Plattnerite PbO_2 indicate that deposition took place from alkaline solutions for which the oxidation potentials are less positive.

As the oxidation potentials become less positive very rapidly with increase in pH, the oxidation proceeds more readily in alkaline solution, cf. $\text{Fe}(\text{OH})_2 \longrightarrow \text{Fe}(\text{OH})_3$

E. Separation of Elements on the Basis of Oxidation Potentials:

Rankama⁹ states that there exist chemical potential differences responsible for the formation of the different minerals in homogenous spheres. Goldschmidt⁷ has shown that if radii, charges and the ionic types of two elements are alike no separation of elements takes place. Zr-Hf, and Yt-Holmium are usually found together. He further shows that if radii are the same but the charges different, the ions having larger charge crystallize more readily. (Example, Sc - vs - Li)

Separation of elements is specially noticed in the upper zone of the lithosphere by the process involving solution and redeposition. In the primary deposits Fe, Co, Ni occur together. Supergene enrichment, a process whereby some metalliferous substances upon weathering are transported chiefly downward by percolating water and are then redeposited, results in their separation. Iron is readily oxidised to trivalent state in alkaline solution; cobalt requires a higher potential even in alkaline medium; nickel requires still higher potential for oxidation. In the supergene deposits, $\text{Fe}(\text{OH})_3$ is common, (Co OOH) occur only under strongly oxidising conditions, whereas higher oxide of nickel is not known to occur as a mineral. Lateritic iron ore in Cuba shows enrichment of iron in the residual deposits; Ni and Co have evidently been removed by solution, on account of their greater stability in divalent state. The natural separation of Fe and Mn ores can be explained in a similar manner, manganese deposits being found comparatively free from iron.

Enrichment of rare elements in oxidising and reducing environment is observed. Environments containing rare elements are characterized either by very high or by very low oxidation potentials. Iodate is found where highly oxidising conditions prevailed along with nitrate deposits. Cu, Pb, V, and U ores are found in sandstone or shales which are far from the igneous source rocks and represent the deposits formed under desert oxidation conditions. These deposits also show marked concentrations of less common elements like Ag, Ni, Co, Cr, Mo, Se, etc. Also, the less widely distributed elements such as Co, Ni, Ga, Ge, Mo, As, etc. are found concentrated on the highly reducing environment furnished by coal deposits. Goldschmidt⁷, 1935, noted the presence of rare elements in coal ashes.

This suggests that sedimentary deposits formed under the strongly oxidising and reducing conditions deserve careful examination for unexpected concentrations of rare elements. Sedimentary deposits in India represent a particular example of enrichment of rare elements in a highly oxidising zone.

F. Geochemical Cycle:

Though not realised in practice one may envisage a geochemical cycle, a) initial crystallization of a magma, b) alteration and weathering c) transportation and deposition, of minerals thus produced, d) diagenesis and e) lithification to f) metamorphism and eventual g) regeneration of magma by antexis and palingenesis. However the processes of oxidation and reduction are distinctly correlated with the stages of cycle. Further study of the subject can bring more light towards solution of many geological problems.

III. Conclusion

The facts of geology indicate that the primary sources of ore deposits are to be found at great depths; these are inaccessible to the action of artificial or natural waters. The hydrothermal theory would require enormous volume of water in the heated crust of the earth to bring the metal values nearer to the surface. From the general facts of science it seems impossible that such an unnatural requirement for so light and volatile a substance as water can prevail. It seems possible that the primary medium was non-aqueous in character involving silica or silicate melts, or that the metals and their compounds migrated towards the earth's surface in vapor state.

The application of oxidation and reduction potentials to geological phenomena assumes existence of an aqueous medium; to date such effects can be found only in sedimentary deposits, in sea or lake water deposits or in places where water played an important role.

IV. References

- 1 Rankama, K., Am. J. Science, 245,458, 1947.
- 2 Clarke, F. W., Data of Geochemistry. Published by U.S.G.S. 1923
- 3 Goldschmidt, Geochemie Naturwiss Handwörterbuch, vol. 4, p. 11 - 19.
- 4 Mason, J. Geol., January, 1949
- 5 Zo Bell, Am. Assoc. Petro. Geologists Bull, No. 30
- 6 Allgeir, Haffard, Juday, Wis. Acad. Sci. Trans., 33,115, 1941
- 7 Goldschmidt, J. Chem. Soc., P. 655, 1937. Ind. Eng. Chem., 27,
1100, 1935
- 8 Chapman and Schweitzer, J. Geol., 55, 43, 1947
- 9 Rankama, K., On the Geochemical Differentiation in the Earth's
Crust. Bull. Com. Geol. Fin., 1946

Leo F. Heneghan

January 17, 1950

I. Study on Reactions of Optically Active Complexes with Optically Active Coordinating Groups

During recent years the researches of Bailar and co-workers have built up evidence for the very interesting phenomenon of "preferential coordination". In some cases the ability of one isomer of a racemic mixture to enter the coordination sphere of an inorganic complex containing optically active coordinating groups was sufficiently different from that of the other isomer so as to permit partial resolution of the racemic mixture. With other racemic mixtures; e.g., racemic amino acids, preferential coordination was not exhibited. The results of these previous investigations seem to indicate that the stabilities of complexes containing amino acids may be too similar to permit preferential coordination. It was the purpose of this research to investigate further the ability of the two isomers of an amino acid to react with cobalt complexes containing optically active propylenediamine. Tyrosine was chosen as the amino acid to be investigated. There seemed to be two logical ways to attack the problem:

- (1) Attempt to resolve tyrosine with bis levo-propylenediamine complexes.
- (2) Study the rate of coordination of each isomer separately in order to obtain quantitative information on the stabilities of the complexes of dextro and levo tyrosine.

In the first set of reactions studied $[\text{Co } \underline{\text{l-pn}_2} \text{Cl}_2] \text{Cl}$ was allowed to react with a 100% excess of racemic tyrosine. If the stabilities of $[\text{Co } \underline{\text{l-pn}_2} \text{d-tyro}] \text{Cl}_2$ and $[\text{Co } \underline{\text{l-pn}_2} \text{l-tyro}] \text{Cl}_2$ are sufficiently different then, in the presence of excess amino acid, the less stable complex should give way to the more stable one giving at least a partial resolution of the amino acid. The second set of reactions involved $[\text{Co } \underline{\text{l-pn}_2} \text{l-tyro}] \text{Cl}_2$, $[\text{Co } \underline{\text{l-pn}_2} \text{d-tyro}] \text{Cl}_2$ and levo-propylenediamine in equimolar ratios. If one isomer of the amino acid is more readily replaced by the active diamine than the other, then partial resolution should result. In neither case was resolution of the amino acid observed.

While this gave qualitative information for the similarities in the coordinating abilities of the two isomers of tyrosine, quantitative data was lacking. Such data was obtained by determining the rates of coordination of dextro and levo tyrosine separately with levo-propylenediamine complexes of cobalt. It was then apparent that the ability of one isomer of the amino acid to coordinate was so similar to that of the other isomer that preferential coordination could not be expected.

The amino acids are known to form relatively stable complexes with cobalt. This strong tendency for the individual isomers to enter the coordination sphere apparently overcomes any directing influence of the levo-propylenediamine complex.

II. Stereoisomers of the Dichloro Bis Ethylenediamine Platinum (IV) Ion

Several investigators have attempted to prepare the stereoisomers of the dichloro bis ethylenediamine platinum (IV) ion but met with little success. In each case the trans isomer was prepared

without difficulty but no definite proof was extended to show that the corresponding cis isomer had been prepared. If a satisfactory synthesis for the cis isomer could be developed, the way would be open for further investigations not only with this but with similar ions containing other negative groups or other diamines.

The usual method for changing a trans isomer of this type to the cis isomer involves conversion to the carbonate derivative with silver carbonate followed by treatment with alcoholic hydrogen chloride. It was found that the coordinated chloro groups were so firmly held by the central metal ion that they could not be removed even upon extended grinding with silver carbonate. Since the bromide ion is larger it should be less firmly held to the central platinum ion and, therefore, should be more easily removed. Also the greater insolubility of the silver bromide formed over that of silver chloride should favor the conversion of trans $[\text{Pt en}_2 \text{Br}_2] \text{Br}_2$ to $[\text{Pt en}_2 \text{CO}_3] \text{CO}_3$. All of the bromide was successfully removed from the coordination sphere with silver carbonate. However, if $[\text{Pt en}_2 \text{CO}_3] \text{CO}_3$ is a product of this reaction, it is certainly very unstable. This was evident both from the change in analytical composition upon standing and the change in color of its aqueous solution.

The next thought was to try to develop a procedure for the direct synthesis of the cis dichloro bis ethylenediamine platinum(IV) ion. Although the work has not been completed it appears that such a synthesis has been developed.

A Polarographic Study of Some Inorganic Complex^s~~es~~

E. I. Onstott

January 17, 1950

Cupric complexes of ethylenediamine, propylenediamine, and diethylenetriamine were found to be reduced reversibly in one step to copper amalgam. The reduction of the glycine complex directly to the amalgam was reversible in the pH range of 6 to 8 when a phosphate buffer was used.

Cupric ion in the presence of pyrophosphate at a pH of 3.6 to 5.3 was found to be reduced reversibly in one step when an acetate buffer was used. However, at higher pH values, the reduction proceeded in two steps, the ratio of the heights of the two waves varying with pH. Reversibility of the electrode reactions was not exhibited. The occurrence of the double wave was attributed to the reduction of two different complex ions in sluggish equilibrium, one being more easily reduced than the other. This interpretation differs from that of Rogers and Reynolds (2), who attributed the double wave to the reduction of a single complex ion, one electron being added in each electrode reaction.

The dipyridyl complex of copper was found to be reduced in two steps. In the first step the corresponding cuprous complex was formed, and in the second step further reduction to the amalgam occurred. Both electrode reactions were reversible.

In the presence of thiourea, the cuprous complex was found to be reduced reversibly in one step to the amalgam. A study of the cupric complex was not possible, as it does not exist under ordinary conditions.

The equations derived by Lingane (1) were used to determine the formulae of the complex ions and to calculate their dissociation constants. Plots of the half-wave potentials of the complex ions versus the logarithm of the concentration of excess complexing agents gave slopes indicative of the number of coordinated groups. Formulae which were determined and dissociation constants which were calculated are listed in the table below.

| <u>Formula</u> | <u>Conc. of excess complexing agent</u> | <u>Calculated Kd</u> |
|---|---|-----------------------|
| $[\text{Cu en}_2]^{++}$ | 40 to 2000-fold | 1.9×10^{-20} |
| $[\text{Cu pn}_2]^{++}$ | 40 to 2000-fold | 6.8×10^{-21} |
| $[\text{Cu dien}_2]^{++}$ | 40 to 2000-fold | 1.4×10^{-21} |
| $[\text{Cu gly}_2]$ | 1 to 10-fold | 7.9×10^{-16} |
| $[\text{Cu diby}_3]^{++}$ | 50 to 200-fold | 1.4×10^{-18} |
| $[\text{Cu diby}_2]^+$ | 50 to 200-fold | 6.3×10^{-15} |
| $[\text{Cu tu}_4]^+$ | 50 to 1600-fold | 4.1×10^{-16} |
| $[\text{Cu}(\text{HP}_2\text{O}_7)_2]^{-4}$ | 1-fold | 1×10^{-10} |
| $[\text{Cu}(\text{HP}_2\text{O}_7)]^-$ | 1-fold | 4×10^{-7} |

Identification of the pyrophosphate complex ions of copper present at pH values greater than 5 was not possible from half-wave potential data, but evidence for the existence of pyrophosphate (monohydrogenpyrophosphate) cuprate (II) ion in the pH range of 7 to 10 was obtained from diffusion current data. The diffusion current constant of bis (monohydrogenpyrophosphate) cuprate (II) ion was found to be about 11% greater than that for the complex ion which exists at a pH of 7 to 10. This difference was attributed to a difference in charges of the two complex ions, assuming their equivalent ionic conductance to be the same.

By determining the pH at which cupric hydroxide was precipitated from solutions containing the pyrophosphate complex ion and excess pyrophosphate ion, it was possible to evaluate an equilibrium constant for the reaction of the complex ion with hydroxide ion to form cupric hydroxide. The complex ion found to be in equilibrium with cupric hydroxide at the pH it is precipitated was hydroxypyrophosphatecuprate (II) ion. Its dissociation constant was calculated to be 2×10^{-16} .

Bis (ethylenediamine) copper (II) ion, normally reduced directly to the amalgam, was found to be reduced in two separate steps when a large excess of ethylenediamine and thiourea, which stabilizes only cuprous ion, were present. In the first step the cupric complex ion was reduced irreversibly to the cuprous complex ion, but further reduction to copper amalgam in the second step took place reversibly, the potential being determined by tetrathiourea copper (I) ion.

Tetrachloroplatinate (II) ion was shown to be reduced at the dropping mercury electrode (contrary to a report by Willis (3)) at small values of applied e.m.f., giving a wave which showed a decreasing current region at more negative potentials. The current decreased to a minimum value before increasing again due to the normal irreversible reduction of tetrachloroplatinate (II) ion. The decrease

in current as the potential was increased, was shown to be caused by a desorption process, adsorption of the reducible ion being a necessary condition for reduction to occur. As the current for the reduction of the adsorbed reducible ion was controlled by a diffusion, an equation describing the desorption wave could be derived by considering the thermodynamics of adsorption equilibrium. The equation which was derived is

$$E = E_{\frac{1}{2}}^d - RT/2F \ln A - RT/2F \ln (i_{d-i})/i,$$

where A represents the average area of adsorption and other symbols are those conventionally used in polarography. Reversibility of the desorption process was tested by finding the slopes of plots of $\log (i_{d-i})/i$ vs. E. The desorption did not appear to be reversible as the slopes of the logarithmic plots were usually about threefold greater than the theoretical value. However, the desorption half-wave potential was independent of the solution tetrachloroplatinate (II) ion concentration, as predicted from the theoretical equation.

The effect of decreasing the average area of adsorption by adding organic materials which are adsorbed on the dropping mercury electrode was studied. It was found that saturated camphor and saturated octyl alcohol shifted the desorption wave marked in the positive direction. Agar and gelatin had a similar but less pronounced effect.

Tetrachloroplatinate (II) ion gave a normal irreversible reduction wave which had a half-wave potential of -1.35 volts (vs. S.C.E.) for one molar potassium chloride indifferent electrolyte. The half-wave potential shifted to more positive values of e.m.f. as the chloride ion concentration was increased.

BIBLIOGRAPHY

1. Lingane, J.J., Chem. Rev., 29, 1 (1941).
2. Rogers, L.B., and Reynolds, C.A., J. Am. Chem. Soc. 71, 2081 (1949), Anal. Chem. 21, 176 (1949).
3. Willis, J.B., J. Am. Chem. Soc., 67, 547 (1945).

The Phosphates and Polyphosphates of the Rare Earths and Thorium

A. G. Buyers

January 17, 1950

Introduction

The investigation of the phosphates and polyphosphates of the rare earths and thorium was undertaken in order to:

- 1.) Identify the phosphate species formed during the opening of an ore such as monazite.
- 2.) Characterize the phosphates and polyphosphates of the rare earths and thorium.
- 3.) Develop a method for the separation of thorium from the rare earths by application of differences in the properties of the respective phosphates and polyphosphates.

I. Orthophosphates of the Rare Earths

A.) Average Atomic Weight Determinations. The reaction, $R^{+3} + H_2PO_4^{-1} \rightarrow RPO_4 \downarrow + 2 H^+$ (pH = 4.5), was investigated in the hope that it might find application for the determination of the average atomic weight of rare earth mixtures. Known weights of rare earth oxide were dissolved in dilute hydrochloric acid and adjusted to a pH of 4.5, an excess of a solution of sodium dihydrogen phosphate

12-11-1914
The first of the series of lectures on the history of the English language was given by Mr. J. H. Green on the 12th inst. at the University of Cambridge. The lecture was attended by a large number of students and was most interesting.

The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting. The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting.

The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting. The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting.

The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting. The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting.

The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting. The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting.

The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting. The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting.

The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting. The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting.

The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting. The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting.

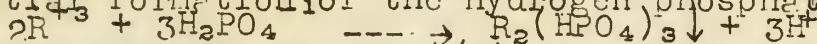
The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting. The lecture was given in the lecture hall of the University of Cambridge. The lecture was attended by a large number of students and was most interesting.

was added, and the released hydrogen ion titrated with standard base. The atomic weight was calculated from;

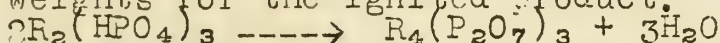
$$\frac{R_2O_3}{4(H^+)} = \frac{\text{Wt. of rare earth oxide}}{(\text{Vol. base})(N \text{ base})(M. eq. wt. H^+)}$$

Values obtained by this method were compared with parallel determinations by the standard permanganate method, (1.) and a new procedure involving a cerate titration of the oxalate in perchloric acid. (2.) The majority of average atomic weight determinations based on the phosphate reaction yielded high results as compared with the permanganate and cerate methods, indicating that quantitative release of hydrogen is not achieved under the given conditions.

B.) Precipitation of Rare Earth Orthophosphates. Results obtained in A.) indicated that precipitates obtained consist essentially of the orthophosphates. Gravimetric determination by drying at 110° C and ignition at 900° C. suggests slight contamination with pyrophosphate assuming some initial formation of the hydrogen phosphate.



This would account for slightly low H^+/R^{+3} ratios and also higher than theoretical weights for the ignited product.

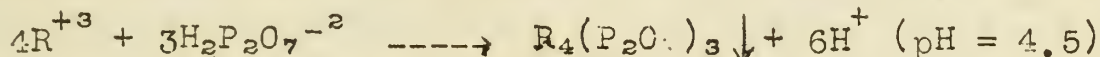


X-ray diffraction patterns of the ignited products are identical with those obtained from finely ground monezite sand in which the rare earth is known to exist as an orthophosphate.

Simultaneous pH and conductometric titration curves of rare earth with di- and trisodium orthophosphate reveal that orthophosphates are precipitated in each instance.

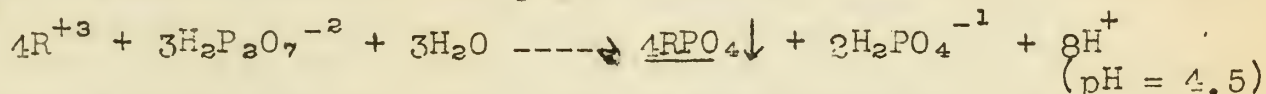
II. Pyrophosphates of the Rare Earths

The technique of back titration of released hydrogen ion to a given pH, i.e., 4.5 was also applied to an investigation of rare earth pyrophosphates. The reaction can be represented by the equation:



The hydrogen ion/rare earth ratio was calculated and found to approximate 1.5 as required by the equation above.

Heating the suspension of the rare earth pyrophosphate in its mother liquor results in conversion of the precipitate to the orthophosphate, either by hydrolysis of the precipitate itself or by hydrolysis of excess pyrophosphate ion and reaction with the precipitate. The reaction representing this change may be indicated by the equation:



The hydrogen ion/rare earth ratio approached that required for quantitative conversion to the orthophosphate.

While initial weights of precipitated pyrophosphate, upon ignition at 900°C. agree closely with theory, long extended heating at this temperature caused weight losses eventually approaching the theoretical weight for an orthophosphate. Such ignited products were found by x-ray diffraction to consist of orthophosphate.

Simultaneous pH and conductometric titrations, involving titration of the rare earth solution with the pyrophosphate demonstrated that the normal rare earth pyrophosphate is formed. However, in the pH range 8.0-10.0, in the presence of a large excess pyrophosphate reagent, a rare earth-pyrophosphate complex ion is formed, whose exact nature has not yet been determined.

THE ... OF THE ...

...

...

...

...

...

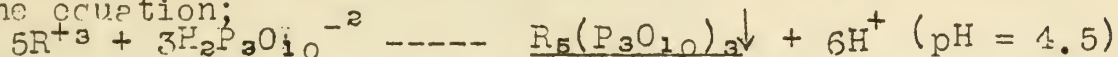
...

...

...

III. Triphosphates of the Rare Earths

The nature of the reaction between solutions of the sodium triphosphate and solutions of rare earth salts using the hydrogen ion displacement procedure discloses that the reaction may be represented by the equation;

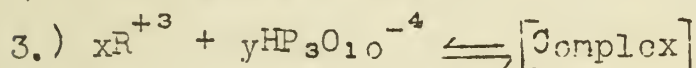
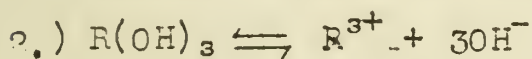
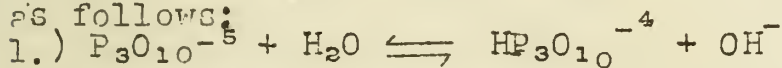


Here again the ratio of released hydrogen ion to rare earth is slightly less than that demanded by theory.

Simultaneous pH and conductometric titrations, titrating the rare earth solution with a solution of sodium triphosphate, and employing the reverse procedure, show that:

- 1.) A normal rare earth triphosphate is formed at a pH of 4.5.
- 2.) In the presence of a large excess of triphosphate reagent and at a pH of 7.0-8.5 a soluble rare earth-triphosphate complex is formed.
- 3.) A rare earth-triphosphate mixture forms no precipitate at a pH of 1.0 on standing for at least one month unless heated.

Rare earth hydroxides are sequestered by excess triphosphate only over a limited pH range. Suspensions of $R(OH)_3$ in triphosphate (pH = 9.5-10.0) can be brought into solution by lowering the pH to 8.0. This suggests competitive equilibria which may be represented as follows:



IV. Trimetaphosphates of the Rare Earths

The information concerning the trimetaphosphates of the rare earths is limited. At a pH of 1.0 the reaction between trimetaphosphate and rare earth ion in solution yields no insoluble product. At higher pH values, a precipitate will form gradually, but the precipitation is not immediate and is not complete even after one week. Precipitate is due to hydrolysis of trimetaphosphate.

V. Ortho-, Pyro-, and Triphosphates of Thorium

Because thorium will precipitate as a hydrous oxide from aqueous solution at a pH above 3.0, it is not feasible to employ the hydrogen ion displacement method used for the rare earths.

A study of the simultaneous pH and conductometric curves, obtained by titration of thorium nitrate solutions with various phosphate reagents (disodium hydrogen phosphate, trisodium phosphate, tetrasodium pyrophosphate, and pentasodium triphosphate.) disclosed that thorium will form a normal salt in each case. Reverse titration of tetrasodium pyrophosphate and pentasodium triphosphate solutions with thorium nitrate revealed that soluble complexes are formed. These complexes are formed at a pH above 6.0 for thorium-pyrophosphate mixtures, and above 5.0 for thorium-triphosphate mixtures.

Thorium ion and triphosphate, both at a pH of 1.0 react to give a gelatinous precipitate of the hydrated triphosphate when mixed.

VI. Trimetaphosphates of Thorium

Thorium nitrate solutions at pH values of 1.0-3.0 yield gelatinous precipitates with aqueous trimetaphosphate at the same pH. The precipitation of thorium is nearly quantitative after a period

of 72 hours. Due to the fact that hydrolysis of trimetaphosphate takes place rapidly in acid solution and the fact that the reaction is not immediate, attempts to determine the composition of the precipitated material have been unsuccessful.

VII. Conclusions

- 1.) The rare earths form normal ortho-, pyro-, and triphosphates under suitable conditions in aqueous solution.
- 2.) The rare earths will form soluble complexes with pyrophosphate in the pH range 8.0-10.0, and with triphosphate in the pH range 7.0-8.5.
- 3.) The rare earths are not precipitated by either triphosphate or trimetaphosphate at a pH of 1.0.
- 4.) Thorium will form normal salts with ortho-, pyro-, and triphosphate under suitable conditions from aqueous solution.
- 5.) Thorium will form a soluble complex with pyrophosphate in the pH range 7.0-10.0, and with triphosphate in the pH range 5.0-6.0.
- 6.) Thorium is precipitated in the form of an insoluble normal triphosphate at a pH of 1.0, also quantitatively by trimetaphosphate after 72 hours.
- 7.) Separation of thorium from the rare earths is theoretically possible by:
 - a.) Precipitation of thorium at a pH of 1.0 using either aqueous sodium triphosphate or trimetaphosphate.
 - b.) Formation of a soluble complex of thorium at a pH above 5.0-6.0, under which conditions the rare earths form insoluble triphosphates.
- 8.) Further work is necessary to determine the nature of the soluble complexes of thorium and the rare earths, and of the precipitation products of both thorium and the rare earths with trimetaphosphate.

References

1. Pearce, Barthauer and Russell, "Inorganic Syntheses", McGraw-Hill Book Co., Inc., 1946, Vol. II, p. 58-61.
2. Smith, G.F., "Cerate Oxidimetry", G. Frederick Smith Chemical Company, Columbus, Ohio, 1942, p. 37-39; 79-82.

INORGANIC COMPLEX COMPOUNDS
CONTAINING POLYDENTATE GROUPS

Allan D. Gott

February 28, 1950

Study of the stereochemical configuration of the quadricovalent complexes of the nickel (II) ion has shown these to be either tetrahedral or planar. Klemm and Raddatz (2) found the complex of nickel (II) with ethylenediamine tetraacetate to be tetrahedral, whereas Morgan and Burstall (3) found the 2:2:2:2:2 tetrapyridyl complex salts of this metallic ion to be planar. Complexes with phthalocyanine (4) and bi-quanide (5) are also planar.

In most of the cases studied the coordinating groups are mono- or bidentate; those involving polydentate coordination were restricted to planar configurations as imposed by the nature of the coordinating group. Jonassen and Douglas (1) have studied the complexes formed between the nickel (II) ion and triethylenetetramine ($\text{NH}_2\text{C}_2\text{H}_4\text{NH}\text{C}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$) and attempted to determine the stereochemical configuration of these complexes. Triethylenetetramine, abbreviated "trien", is unique in that it can orient itself with little strain around a metallic ion exhibiting either tetrahedral or planar bond direction (1), (10). A study of such complexes might shed light on the ease of conversion of nickel (II) complexes from tetra- to hexacoordination since Dwyer and Mellor (6) found that planar diamagnetic tetra complexes showed little tendency to assume hexacoordination whereas the tetrahedral paramagnetic complexes could easily convert to the octahedral configuration by taking up two more donor groups.

Spectrophotometric studies were made on solutions of known concentrations of nickel (II) chloride and trien. Both absorption data and data from continuous variation studies (7) indicate clearly that a 1:1 complex $[\text{Ni}(\text{trien})]^{+2}$ and a 2:3 complex $[\text{Ni}_2(\text{trien})_3]^{+4}$ (1) are formed. Only the $[\text{Ni}_2(\text{trien})_3]^{+4}$ ion could be isolated. It was suggested (1) that a conversion of the 1:1 complex to the 2:3 complex takes place readily. The salts of the latter ion show octahedral configuration but all attempts at resolution failed. Explanations can be presented for this failure, the more preferable being that either the meso forms were the only ones present in the solution or that the bonds are predominately ionic and racemization occurs rapidly. Magnetic studies of the 2:3 complex salts indicate the presence of two unpaired electrons.

Jonassen and Cull (8) subsequently studied the complex ions formed between trien and the platinum (II) and palladium (II) ions. Previous evidence indicates that both of these metallic ions complex through a planar configuration (9). Complexes with triethylenetetramine should provide further proof of this. In a tetrahedral complex paramagnetism should be produced by unpaired electrons. This type of complex should also be resolvable if the linkages are mainly covalent (8).

Absorption studies for both the platinum (II) and palladium (II) systems indicate the formation of one or more colored complexes in each case. Continuous variation studies failed to be of value. The metallic tetrachloro complexes and their conversion to triethylenetetramine complexes showed little difference in absorption characteristics (8). The data indicate a 2:1 Magnus-type salt of the formula $[\text{Pt} \text{ trien}] [\text{PtCl}_4]$.

Large optically active anions were employed in an effort to precipitate the 1:1 complexes of both platinum (II) and palladium (II), but all attempts failed. Since no platinum was present in the salt fractions isolated it was assumed that the resolving agents (d-tartaric acid and d- α -bromocamphor-7 β -sulfonate) were more insoluble than the platinum salts (8).

The magnetic properties of complex salts of both platinum (II) and palladium (II) of the type $[\text{Pt}(\text{trien})][\text{Pt Cl}_4]$ were studied. They were found to be diamagnetic, in complete agreement with the expected planar configuration.

BIBLIOGRAPHY

1. Jonassen and Douglas, J. Am. Chem. Soc., 71, 4094 (1949).
2. Klemm and Raddatz, Z. anorg. allgem. Chem., 250, 204 (1942).
3. Morgan and Burstall, J. Chem. Soc. 1672 (1938).
4. Woodward, J. Chem. Soc. 601 (1940).
5. Ray and Ray, J. Indian Chem. Soc. 21, 163 (1944).
6. Dwyer and Mellor, J. Am. Chem. Soc., 63, 81 (1941).
7. Vosburgh and Cooper, ibid, 63, 437 (1941).
8. Jonassen and Cull, ibid, 71, 4097 (1949).
9. Mellor, Chem. Rev. 33, 137 (1943).
10. Basolo, J. Am. Chem. Soc. 70, 2634 (1948).

CHEMISORPTIVE BONDS AND CATALYSIS

S. M. Cohen

February 28, 1950

INTRODUCTION

Although the idea of chemical bonding in chemisorptive linkages is inherent in the term "chemisorption", little is known of the nature of such bonds. The subject is of special interest in connection with the mechanism of contact catalysis where, in many cases, various components of a system undergoing catalysis become associated with a solid catalyst by the formation of chemisorptive bonds. In analyzing some of the factors which produce this type linkage, it is obvious that the structures of both the substances which are adsorbed and the catalyst itself must be considered. This applies to hydrogenation and other types of contact catalysis where, for various reasons, it appears that chemical bonding rather than general adsorption by van der Waals forces is involved. (13)

A convenient approach to this subject can be found by a study of catalyst poisoning, since the occurrence of this toxicity constitutes an easily recognizable indication of a strong bond. It is known that strong bonds are formed with metallic hydrogenation catalysts of the three transition groups represented by Ni, Pd, and Pt, as with their neighbors, by several general types of substances. These would include (1) molecules containing S, Se, Te, P, As, or Sb; (2) a large number of metallic ions; and (3) substances containing certain unsaturated bonds, such as CO, $-C\equiv N$ compounds, or $CH_2=CH_2$. (13)

CORRELATION BETWEEN CATALYTIC ACTIVITY AND MAGNETIC PROPERTIES

In considering the adsorbing metals, it is interesting to compare the three groups of transition elements employed for catalytic hydrogenation. If these are set down in order of increasing atomic number, it can be seen that those metals which are ordinarily associated with the most effective catalytic properties for hydrogenation fall under one another and that their observed activities appear to vary in each horizontal series in such a way that the activity rises to a maximum at the elements enclosed in the frame and then falls steeply, in that Cu, Ag, and Au - all of which have a completely occupied d shell - possess a low or even zero activity for catalytic hydrogenation. (13)

| | | | |
|----|----|----|----|
| Fe | Co | Ni | Cu |
| Ru | Rh | Pd | Ag |
| Os | Ir | Pt | Au |

Furthermore, it is of interest to note that this activity sequence is followed by the compared values of the paramagnetic susceptibility, at least in the two groups where these measurements are less complicated by ferromagnetism. Since this was determined by the structure of the d-band, the apparent connection between activity and paramagnetic susceptibility seems to indicate that the catalytic activity is determined by the structure of the d band; and, above all, the disappearance of catalytic properties with the disappearance of fractional electron deficiencies in this band strongly suggests that these deficiencies play a critical part in the hydrogenation catalysis and in adsorption connected with this. (13).

TOXICITY OF NON-METALS OF GROUPS VA AND VIA

In the case of catalyst poisons of the S or P class, it has been found that toxicity is dependent on the presence of free electron pairs in the valency shell of the toxic element. These are evidently necessary for the formation of the link with the catalyst, since the toxicity (i. e. the ability to form a relatively strong chemisorptive bond) disappears if the structure of the molecule is such that the normally toxic element possesses a completely shared electron octet. Thus, organic sulfides or thiols are toxic towards a Pt catalyst whereas sulfones or sulfonic acids are not: (13)

Indications have been found (12), by means of magnetic measurements, that electrons from, for example, methyl sulfide probably enter the d-band of the adsorbing metal to give a coordinate link, the process possibly being accompanied by an elimination of any fractional electron deficiencies in the d-band of the metal due to d-s₊ band overlap. The adsorption complex formed may be written as $M \leftarrow S(CH_3)_2$. (13)

A further indication of this toxicity rule is seen from the fact that (11) a N atom containing a free electron pair can be catalytically toxic. As an illustration, very carefully dried NH₃ in cyclohexane solution has been found to be toxic towards a Pt catalyst, whereas NH₄⁺ is not toxic under the same conditions. (13)

TOXICITY OF METALLIC IONS

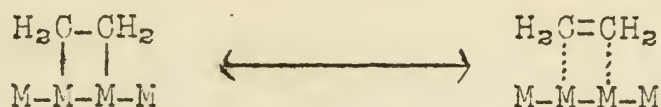
The poisoning of Pt or similar catalysts by toxic metal ions falls into a somewhat different category, since the adsorption complex probably resembles an intermetallic compound. Here the toxicity appears to be confined to those metals in which all five orbitals of a d shell, which is immediately followed by s or p valency orbitals, contain at least one electron each. (10,13) Since no toxicity is observed if unoccupied d orbitals, or no d orbitals at all, are present, it seems probable that d electrons are in some way concerned in the intermetallic bond between the toxic metal and the catalyst. The toxic metals thus differ from the non-metallic elements of Groups VA and VIA by the type electrons which they contribute to the transition metal catalyst. The non-metallic elements of Groups VA and VIA, as contrasted with the toxic metals, can apparently form strong bonds with their s and p valency electrons. (13)

The evidence that these strongly adsorbed ions, themselves, act as the effective poisons, as opposed to the idea that they first undergo a change into a metallic deposit, lies largely in the observed reversibility of the adsorption, i. e. the existence of a well-defined adsorption-desorption equilibrium. (13)

STRONGLY ADSORBED SUBSTANCES CONTAINING UNSATURATED BONDS

A third condition for strong adsorption by a transition-group metal seems to be the possession of an unsaturated bond. This class of adsorbate is of considerable importance since it includes normal reactants the type of substances which are most usually subjected to catalytic hydrogenation—as opposed to extraneous catalyst poisons. In the adsorption of a molecule containing an unsaturated bond, a new possibility arises in that, in place of the formation of some type of normal covalent bond by interaction with the electron system of the metal, the adsorption may take place by the participation of the metal in a resonance

system of the multiple bond type. This type of bond seems particularly probable ~~for~~ adsorbates which are already strongly resonant, e.g. CO; but it is also possible for ethylene, which, in its unadsorbed state has a low or non-existent multiple bond resonance. This can be illustrated as:



Here, too, from analogy to the previous material, it would be expected that this bonding would be with the d-band of the metal. (13)

Bibliography:

1. Maxted, E. B., J. Chem. Soc., 121, 1760-5 (1922)
2. Maxted, E. B., *ibid*, 127, 73-7 (1925)
3. Ipatiew, W., and Ipatiew, W., Jr., Ber., 60, 1982-6 (1927)
4. Ipatiew, W., and Ipatiew, W., Jr., *ibid*, 61, 624-30 (1928)
5. Ipatiew, W., and Nikolajew, W., *ibid*, 61, 630-4 (1928)
6. Ipatiew, W., and Rasuwajew, G., *ibid*, 61, 634-7 (1928)
7. Maxted, E. B., and Evans, H. C., J. Chem. Soc., 1938, 2071-8
8. Twigg, G. H., and Rideal, E. K., Proc. Roy. Soc., 171 A, 55-69 (1939)
9. Maxted, E. B. and Morrish, R. W. D., J. Chem. Soc., 1940, 252-6
10. Maxted, E. B., and Marsden, A., *ibid*, 1940, 469-74
11. Maxted, E. B., and Walker, A. G., *ibid*, 1948, 1093-7
12. Dilke, M. H., Eley, D. D., and Maxted, E. B., Nature, 161, 804 (1948)
13. Maxted, E. B., J. Chem. Soc., 1949, 1987-91

SYNTHESIS GASES

Homer J. Birch

March 7, 1950

INTRODUCTION

The production, separation, and purification of gases for synthesis purposes is a fundamental step in many chemical operations. To prepare gases of sufficient purity in the quantities needed, requires a consideration of inorganic chemistry as well as chemical engineering and physical chemistry aspects. Coal, natural gas, and petroleum are used as raw materials in the preparation of these gases.

PRODUCTION

Coal or coke is used as the fuel in the producer gas unit. In this process, air and superheated steam are alternately blown through the incandescent carbon. The approximate composition of the gases produced is:

| | "Blow-run" | "Blue gas" |
|-----------------|------------|------------|
| CO ₂ | 10.6% | 13.0% |
| CO | 32.1 | 50.3 |
| O ₂ | 0.2 | 0.3 |
| H ₂ | 5.0 | 33.7 |
| CH ₄ | 0.3 | 1.0 |
| N ₂ | 52.0 | 1.7 |

Other minor constituents are: Tar, NH₃, higher hydrocarbons, olefins, NO, HCN, and sulfur, in both inorganic and organic forms.

Natural gas is reformed by conversion with CO₂ and steam over catalyst. Petroleum fractions are utilized to produce the lower hydrocarbons and olefins by cracking processes.

The catalysts used for these reforming steps consist of mixtures of metallic oxides or sulfides, those of Fe, Co, and Ni being most common, with Cu, MgO, ZnO, and K₂O added as promoters. As trace impurities can affect the catalytic value, their exact composition is important.

SEPARATION AND PURIFICATION

Separation of the gas mixtures can be brought about by selective solubilities, fractional liquifaction and distillation, conversion, or chemical combination and adsorption. The major separation method is selective solubility under moderate pressures. At 30-40 atmospheres water, caustic, and copper ammonium formate solutions are used to separate the producer gases. Further separation is achieved by successive let-down steps in pressure.

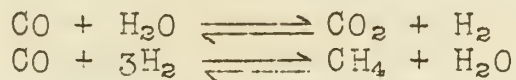
Coke oven gas is usually fractionated by partial liquifaction. By these methods the following purities can be obtained:

| | |
|-------------------------------|-------|
| CO ₂ | 99.9% |
| CO | 98.0% |
| H ₂ | 99.5% |
| C ₂ H ₄ | 99.5% |

The minor impurities are often more difficult to remove. Sulfur and its compounds are removed by Fe₂O₃, "Thylox" arsenite, sodium phenolate, ethanol amine, N-potassium methylglycine, as well as other absorbants. Activated carbon is used to remove unsaturates, and other organic vapors. Since sulfur poisons many synthesis

catalysts, its complete removal is essential, a limit of 0.1 grain per 100 cubic ft being specified. In gases being liquified, NO removal is necessary as it will accumulate in the system.

Conversion or "shifter" units are used to change the CO-H₂ ratios. Depending upon temperature and pressure the reversible reactions are:



Higher temperature and pressure favors the "methanation" reaction which is used to remove trace amounts of CO in pure H₂. The shifter unit will convert blue gas to the following composition:

| | |
|-----------------|-------|
| CO ₂ | 41.2% |
| O ₂ | 0.2 |
| H ₂ | 51.6 |
| CO | 4.6 |
| R | 2.4 |

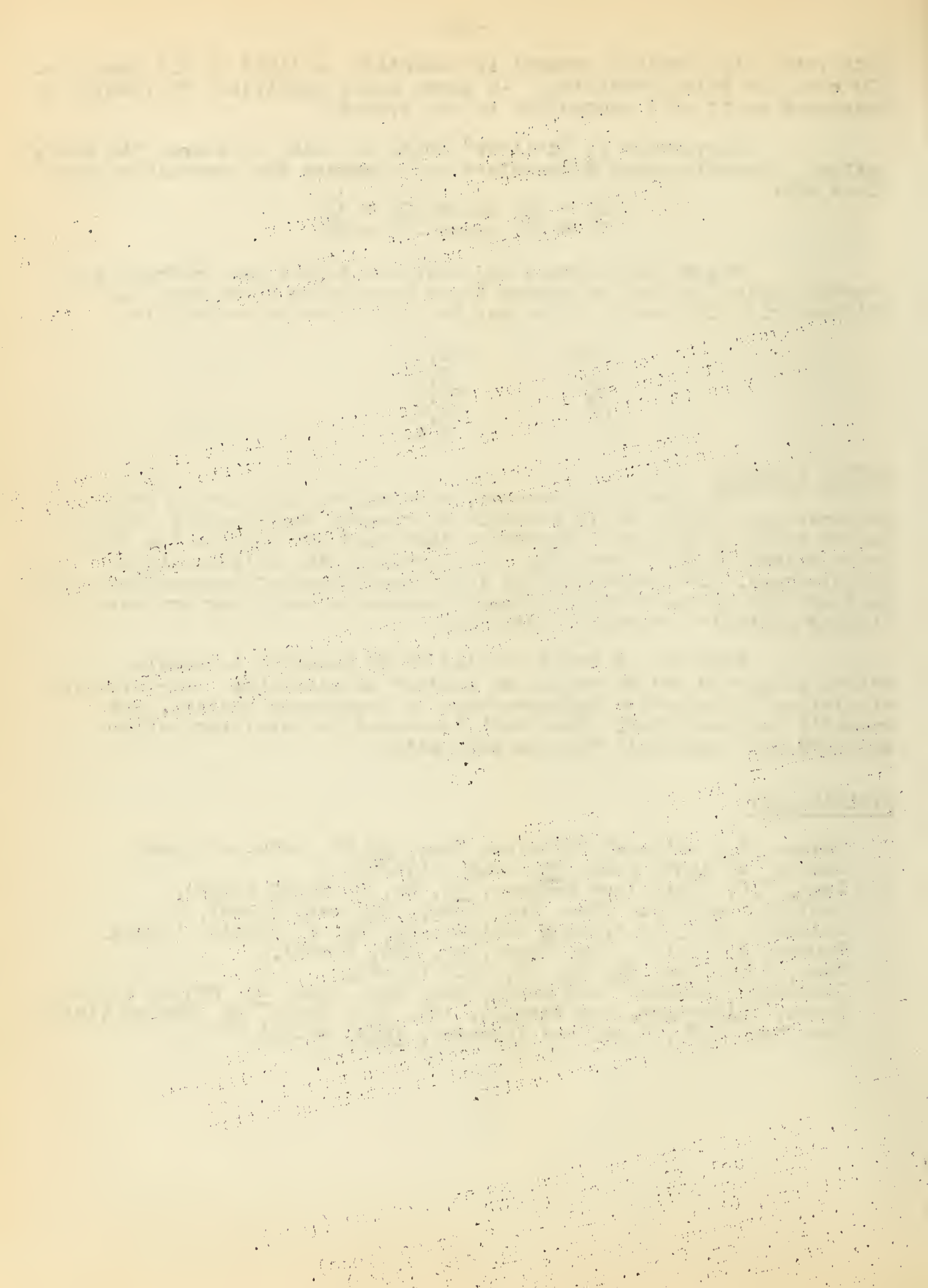
RECENT ADVANCES

The advent of low-cost, pure oxygen has changed the producer gas cycle. It is possible to operate continuously, blowing O₂ and steam to produce a synthesis that does not contain the large inert volume of N₂. Where NH₃ is not being made, this is highly advantageous. The production of large quantities of hydrocarbons from coal and oil by the Fischer-Tropsch process is requiring new work in finding suitable separation methods.

Research is being carried on by industry to develop better catalysts which are not as subject to poisoning. Purification of olefins by selective hydrogenation of acetylenes therein, has recently been achieved. More work is needed in obtaining better solvents and absorbents for gas separation.

BIBLIOGRAPHY

- Cotton, E., National Petroleum News, 38 23, R425-34 (1946).
 Gordon, J. Inst. Fuel, 21, 53-61, (1947).
 Lane, J.C., Petroleum Refiner, 25, No. 8, 87-98 (1946).
 Mayland, and Hays, Chem. Eng. Prog., 45, 452, (1949).
 Mitchell, G.S., Petroleum Refiner, 25, No. 6, 245-49, (1946).
 Newman, L.L., Ind. Eng. Chem., 40, 559, (1948).
 Reed, R.M., Gas, 24, No. 10, 53-6 (1946).
 Reitmeier, Bennett, and Baugh, Ind. Eng. Chem., 40, 620-6, (1948).
 Sands, Wainwright, and Schmidt, Ind. Eng. Chem., 40, 607-20, (1948).
 Schuften, P.M., Chem. and Industry, 1948, 99-104.



THE PEROXY COMPLEXES OF PLUTONIUM(IV)

Richard L. Dalton

March 7, 1950

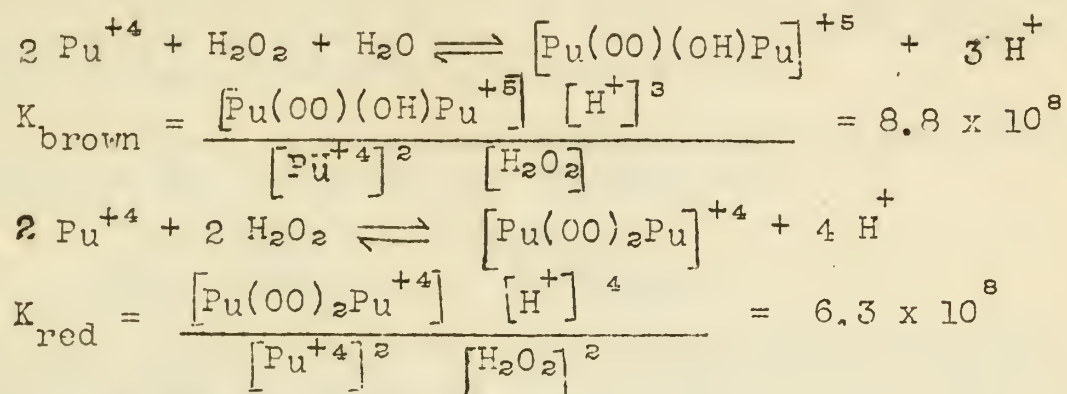
Solutions of plutonium containing hydrogen peroxide possess a pink color indicating some sort of complex formation. In view of the complicated interaction of hydrogen peroxide with plutonium in its various oxidation states, some mention must be made of these effects before discussing the complexes formed by plutonium(IV)

Hydrogen peroxide reduces plutonium(VI) to plutonium(V) at a measurable rate in 0.5M HCl (1). Plutonium(V) is reduced slowly by hydrogen peroxide. However, in solutions containing about $10^{-3}M$ $Pu(V)$, or greater, reduction proceeds by the simultaneous disproportionation of plutonium(V) to give plutonium(VI) and plutonium(IV) or plutonium(III), and the reduction of plutonium(VI) by hydrogen peroxide to plutonium(V). Plutonium(IV) is reduced to plutonium(III) by hydrogen peroxide at a measurable rate in dilute HCl, $HClO_4$, and HNO_3 . Under certain conditions plutonium(III) may be oxidized to plutonium(IV) by hydrogen peroxide. Therefore in a system containing plutonium(IV) and hydrogen peroxide the net reaction is the catalytic decomposition of hydrogen peroxide. In 0.5M HCl the steady state is shifted far toward plutonium(III) so that only a few per cent of plutonium(IV) is present. This equilibrium, however, is shifted toward plutonium(IV) by an increase in hydrogen peroxide concentration due to the formation of complexes with the +4 plutonium. If H_2SO_4 is used instead of HCl, the equilibrium is shifted in the same way, again because of complex formation, with the result that dilute H_2O_2 oxidizes plutonium(III) in H_2SO_4 rapidly and nearly completely to plutonium(IV). At higher concentrations of hydrogen peroxide plutonium(IV) is precipitated. Using an oxidation-reduction titration method the number of peroxide oxygen atoms precipitated with one atom of plutonium has been determined (2). The results correspond to the empirical formula, $PuR_{0.85}O_{3.15}$, where R represents a univalent anion; the suggested formula for the compound is $Pu_2R_2O_6$. Harvey, et.al. (3) report a ratio of peroxidic oxygen atoms to plutonium of 3:2 in the precipitate obtained in H_2SO_4 solution.

When only a small amount of hydrogen peroxide is added to a light brown solution of plutonium(IV), the color changes to a dark brown within a few seconds. The solution becomes red upon the addition of more hydrogen peroxide. The oxidation state of the plutonium must be +4, as reduction to +3 would be indicated by the liberation of oxygen, and hydrogen peroxide could not oxidize plutonium(IV) to plutonium(V) or (VI). Using spectrophotometric data, Connick and McVey (4) were able to calculate the concentration of plutonium(IV), plutonium(III), the brown complex, and the red complex. By varying the plutonium(IV) concentration and the hydrogen peroxide concentration separately, they were able to determine the powers to which these concentrations must be raised in the equilibrium expressions for the complexes. They conclude that the brown complex consists of two Pu^{+4} ions and one peroxide ion. Measurements of e.m.f. confirmed the 2:1 ratio.

By a study of the hydrogen ion dependence of the equilibrium between Pu^{+4} , the brown complex, and hydrogen peroxide, the authors conclude that approximately one hydroxide group is associated with each ion-molecule of the brown complex in 0.5M HCl.

By similar experiments it was determined that the red complex consists of two Pu^{+4} ions and two peroxide ions. These observations may be represented by the following equations and equilibrium constants:



The authors have assumed that no chloride ions are involved in the complexes, since chloride ions complex Pu^{+4} only weakly in the absence of hydrogen peroxide; this tendency should be even less evident with negative peroxide ions already bound to the Pu^{+4} ions.

No evidence was obtained for complexes containing one plutonium atom, even though the concentration of plutonium(IV) was very low throughout the experiments. It is suggested that the great stability of the complexes containing two plutonium atoms relative to those containing one is due to a double bridge structure in the former. A consideration of bond angles and distances indicates that such a structure is possible.

References

1. Connick, R.E.: J. Am. Chem. Soc. 71, 1528-33 (1949).
2. Hopkins, H.H. Jr.: Manhattan District Report, CN-1946, p. 21, August 1, 1944.
3. Harvey, B.G., Heal, H.G., Maddock, A.G., and Rowley, E.L.: J. Chem. Soc. 1947, 1010-21.
4. Connick, R.E. and McVey, W.H.: J. Am. Chem. Soc. 71, 1534-42 (1949).

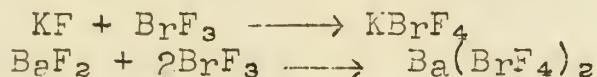
REACTIONS OF BROMINE TRIFLUORIDE

L. F. Audrieth

February 21, 1950

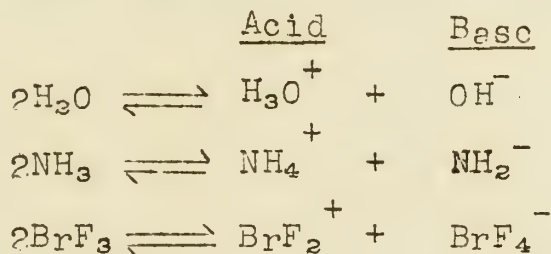
Bromine trifluoride can be prepared readily by the direct reaction between liquid bromine and fluorine (m. 8.8° , b. 127°). The critical temperature is 327° ; $\Delta H_v = 10$ kcal; Trouton's constant, 25.3. (See Reference 1 for preparation and properties).

A number of metallic fluorides will dissolve in BrF_3 , from which compounds such as the following may be isolated:

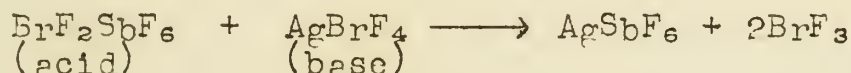


These substances possess characteristic X-ray powder diagrams. When heated, BrF_3 is given off at about 200° . Some of the bromofluorides (?) (better names: fluobromites, tetrafluobromides) lose BrF_3 so readily, e.g., $\text{Ca}(\text{BrF}_4)_2$, that they cannot be isolated in the free state.

Emeleus², who reported the results of this investigation at the symposium on "Fluorine Chemistry" at the Chemical Society meeting in London on November 30, 1949, considers the tetrafluobromides to be base analogs in a BrF_3 system of compounds and assumes auto-ionization to proceed in accordance with the following equations:



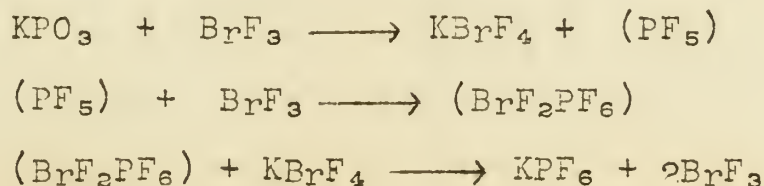
The corresponding "acids" containing the BrF_2^+ cation have been prepared, the compounds BrF_2SbF_6 and $(\text{BrF}_2)_2\text{SnF}_6$ being typical. Conductimetric titrations of these "acids" with "bases" have been made:



The acid BrF_2AuF_4 decomposes at 180°C to give the hitherto unknown AuF_3 . A precipitate of AgAuF_4 is formed instantaneously in the following reaction:



Potassium metaphosphate reacts with BrF_3 to give hexafluorophosphates in good yield. The mechanism of this reaction is postulated as follows:



Hexafluoroarsenates and hexafluoroaurates can be prepared by analogous methods.

One of the reactions described was that in which BrF_3 reacts with NO_2 and a halide, oxide or metal. The products in each case are the corresponding nitronium compounds containing the ion NO_2^+ :

| <u>Reactants</u> | <u>Products</u> |
|--|-------------------------------|
| $\text{SnF}_4, \text{NO}_2, \text{BrF}_3$ | $(\text{NO}_2)_2\text{SnF}_6$ |
| $\text{As}_2\text{O}_3, \text{NO}_2, \text{BrF}_3$ | NO_2AsF_6 |
| $\text{Au}, \text{NO}_2, \text{BrF}_3$ | NO_2AuF_4 |

It is quite probable that the nitronium complexes will act as nitrating agents.

References:

- 1) Simons, Inorganic Syntheses III, 184 (1950).
- 2) Emeleus, Abstract of paper in the Jan. 15, 1950, issue of European Scientific News, Office of Naval Research.

THE DISSOLUTION OF ALUMINUM IN SODIUM HYDROXIDE SOLUTIONS

Donald P. Hallada

March 14, 1950

A number of conflicting reports concerning the mechanism of the dissolution reaction of aluminum in sodium hydroxide solutions have appeared in the literature (1-6). The first comprehensive study leading to reproducible results and permitting correlation of the observed phenomena has appeared only recently (7, 8).

Disks of aluminum, after pre-treatment to remove oxide films, were suspended in a large excess of the test solution. Close temperature control was maintained in all experiments. The rate of dissolution was determined by weight loss. Electrode potential measurements of these systems, under varying conditions, were made.

The weight loss rate was found to increase slightly during the first 180 minutes at all temperatures, but later became constant. During the dissolution process the surface of the test piece was progressively covered by a black precipitate until the metallic surface could be detected through the pores of the precipitate only under a microscope.

Increasing quantities of impurities increased the rate of dissolution. Iron produced the greatest effect. The maximum increase represented the solubility limit of iron in solid aluminum. The impurities form the coating on the surface of the aluminum during the dissolution process. An alloy containing 2.5% magnesium and 0.25% chromium had a constant dissolution rate since the impurities did not form a coating, but dropped to the bottom of the vessel. The electrode potential of the above alloy remained constant during the time of reaction, whereas the potential of alloys which form a surface coating become more cathodic with time.

Addition of small amounts of iron or copper compounds to the solutions increased the rate of dissolution by the formation of a precipitate on the aluminum. Iron was the most effective.

The rate of dissolution was found to reach a maximum when the concentration of sodium hydroxide was 5.5 normal. At greater concentrations the rate of dissolution decreases. Increased concentration of the sodium hydroxide solution resulted in a more negative potential, while raising the temperature made the potential more positive.

The effect of temperature on the rate of dissolution may be represented by the Arrhenius equation: $\frac{dw}{dt} = Ae^{-E/RT}$ where the "experimental energy of activation", E , increases with increasing concentration of sodium hydroxide.

The effect of an external current was studied, using the test disks as both anodes and cathodes. External current caused a slight initial decrease in weight loss rate at the cathode, the weight loss rate then remained constant for higher current values. The weight loss rate at the anode remained almost constant for low external currents, then increased at a constant rate up to about 2.5 m.a./cm.², and then increased more rapidly with increased external current. Under the latter conditions dissolution was solely a function of the external current.

The proposed mechanism follows: The impurities in the aluminum form the cathode of local cells of which the aluminum is the anode. The black precipitate which forms on the surface of the aluminum acts as a cathode, its growth increases the cathodic area, increasing the current density of the local anodes, thus also increasing dissolution rates. The increasing anodic current density causes anodic polarization toward more positive potentials. The cathodic processes predominate in control of the dissolution reaction. The rate controlling step has the properties of a homogeneous chemical reaction, and is probably one step in the transfer of hydrogen ions to hydrogen gas. When the aluminum is made cathodic by an external current the cathode does not polarize since the rate of dissolution is decreased only slightly. When the aluminum is made anodic, the local anodes are polarized, and thus the potential difference of the local cells is gradually decreased with increasing external current. When the local anodes have been polarized to the open-circuit potential of the local cathodes, local cell action ceases, and the weight loss is then electrochemically equivalent to the quantity of current passing through the cell.

BIBLIOGRAPHY

1. Brown and Mears, Trans. Electrochem. Soc., 74, 495 (1938)
2. Centnerszwer, Z. Electrochem., 37, 598 (1931)
3. Tammann and Neubert, Z. anorg. u. allgem. Chem., 201, 225 (1931)
4. Hedges and Myers, J. Chem. Soc., 125, 604 (1924)
5. Centnerszwer, Z. physik. Chem., 131, 214 (1927)
6. Schikorr, Z. Electrochem., 37, 610 (1931)
7. Streicher, J. Electrochem. Soc., 93, 285-315, (1948)
8. Streicher, J. Electrochem. Soc., 96, 170-194, (1949)

THE STRUCTURE OF PENTACOVALENT COMPOUNDS

Arthur M. Ross

March 14, 1950

Pentacovalent compounds have long been known, but determination of their structure has been hampered by their instability and reactivity. The most common structure reported for compounds exhibiting coordination number five is the trigonal bipyramid. In fact, positive experimental evidence to indicate any other pentacovalent structure does not appear to have been published prior to 1949.

A theoretical treatment of coordination number five based on group theory has been presented by G. E. Kimball (1). Of the four possible configurations (trigonal bipyramid, square pyramid, pentagonal pyramid, and plane pentagon), Kimball points out that those structures in which the ligands form a pentagonal plane would be unstable because of strong mutual repulsion of the coordinated groups. Kimball further states that the trigonal bipyramid structure would be expected when dsp^3 and d^3sp bonding is involved, and that d^2sp^2 , d^4s , d^4p , and d^2p^3 bonding would give a square pyramid configuration. These predictions are in accord with experimental determinations of the structures of compounds exhibiting dsp^3 bonding. For example, the structures of both PCl_5 and $Fe(CO)_5$ vapors have been found by electron diffraction to be bipyramidal (2, 3). As an example of a molecule which should have a square pyramidal structure, Kimball specifically cites IF_5 in which the expected valence configuration is p^3d^2 .

Pauling (4) and Sidgwick and Powell (5) postulate that pentacovalent compounds, such as IF_5 , in which the central atom possesses an unshared pair of electrons should exhibit a square pyramidal structure. The unshared pair could then occupy a position directly opposite the vertex of the pyramid, thus forming an octahedron. Although he agrees that this is a possibility, Wells (6) points out that the electron pair may be stereochemically inert.

In view of these theoretical predictions, structural studies on IF_5 should be of considerable interest. The first investigation was that of Braune and Pinnow (7) who studied electron diffraction patterns of IF_5 vapor, but, because of the low relative scattering power of fluorine, could draw no conclusions regarding the structure. They found no evidence, however, to contradict a trigonal bipyramidal arrangement analogous to that of PF_5 . These results were questioned by Rogers, Wahrhaftig and Schomaker (8) on the basis of more recent electron diffraction experiments which showed definitely that the bipyramidal configuration is not correct. These workers also were unable to obtain positive results because of the large difference between the atomic numbers of fluorine and iodine.

A positive determination of the structure of IF_5 , based on interpretation of Raman and infrared spectra, has recently been carried out by R. C. Lord and co-workers (9) at M.I.T. The results of this latest investigation indicate a square pyramidal configuration. The data show definitely that the structure cannot be bipyramidal or pentagonal planar. The results are almost as conclusive regarding the pentagonal pyramidal structure which the authors regard as highly improbable although it cannot be rigorously excluded.

August 10, 1945

Page 1 of 2

The following information was obtained from the records of the War Relocation Authority, and is being furnished to you for your information. It is requested that you keep this information confidential, and not discuss it with any other person.

The information pertains to the activities of the Japanese American Citizens League (JACL) during the war years. The JACL was organized in 1942, and its purpose was to represent the interests of Japanese American citizens who were interned in the War Relocation Authority camps. The JACL was active in many ways, including the collection of funds for the War Relocation Authority, the organization of cultural and educational activities, and the representation of Japanese American citizens before the War Relocation Authority and the War Relocation Authority's Board of Directors.

The JACL was also active in the collection of funds for the War Relocation Authority. It was one of the largest contributors to the War Relocation Authority's fund-raising efforts. The JACL's fund-raising efforts were successful in raising millions of dollars for the War Relocation Authority, which was used to pay the costs of the internment camps and the care of the internees.

The JACL was also active in the organization of cultural and educational activities. It organized many cultural events, including plays, musicals, and dances. It also organized many educational activities, including classes in English, Japanese, and other subjects. The JACL's cultural and educational activities were very popular with the internees, and they helped to keep the internees occupied and happy during their internment.

The JACL was also active in the representation of Japanese American citizens before the War Relocation Authority and the War Relocation Authority's Board of Directors. It was one of the most effective representatives of the internees, and it was able to secure many important concessions for the internees. The JACL's representation of the internees was very successful, and it was a major factor in the improvement of the internees' conditions.

The JACL's activities were very successful, and it was a major factor in the improvement of the internees' conditions. The JACL was also active in the collection of funds for the War Relocation Authority, and it was one of the largest contributors to the War Relocation Authority's fund-raising efforts. The JACL's fund-raising efforts were successful in raising millions of dollars for the War Relocation Authority, which was used to pay the costs of the internment camps and the care of the internees.

The JACL was also active in the organization of cultural and educational activities. It organized many cultural events, including plays, musicals, and dances. It also organized many educational activities, including classes in English, Japanese, and other subjects. The JACL's cultural and educational activities were very popular with the internees, and they helped to keep the internees occupied and happy during their internment.

The JACL was also active in the representation of Japanese American citizens before the War Relocation Authority and the War Relocation Authority's Board of Directors. It was one of the most effective representatives of the internees, and it was able to secure many important concessions for the internees. The JACL's representation of the internees was very successful, and it was a major factor in the improvement of the internees' conditions.

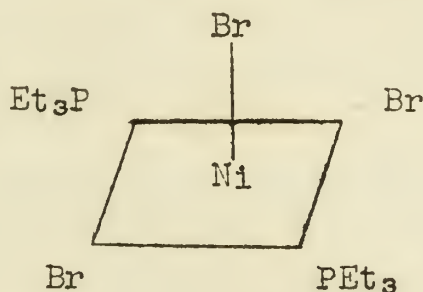
The JACL's activities were very successful, and it was a major factor in the improvement of the internees' conditions. The JACL was also active in the collection of funds for the War Relocation Authority, and it was one of the largest contributors to the War Relocation Authority's fund-raising efforts. The JACL's fund-raising efforts were successful in raising millions of dollars for the War Relocation Authority, which was used to pay the costs of the internment camps and the care of the internees.

The JACL was also active in the organization of cultural and educational activities. It organized many cultural events, including plays, musicals, and dances. It also organized many educational activities, including classes in English, Japanese, and other subjects. The JACL's cultural and educational activities were very popular with the internees, and they helped to keep the internees occupied and happy during their internment.

The JACL was also active in the representation of Japanese American citizens before the War Relocation Authority and the War Relocation Authority's Board of Directors. It was one of the most effective representatives of the internees, and it was able to secure many important concessions for the internees. The JACL's representation of the internees was very successful, and it was a major factor in the improvement of the internees' conditions.

The compound $\text{NiBr}_3(\text{Et}_3\text{P})_2$, exhibiting the square pyramidal configuration, has recently been studied by Jensen and Nygaard of the University of Copenhagen (10). It was shown by molecular weight and magnetic moment measurements to be a monomolecular species exhibiting coordination number five.

The square pyramidal structure was proposed on the basis of dipole moment measurements in benzene solution ($\mu = 2.3\text{--}2.7$ Debye units). Ignoring the possibility of a pentagonal configuration, Jensen and Nygaard consider only the trigonal bipyramid and square pyramid as possible structures for $\text{NiBr}_3(\text{Et}_3\text{P})_2$. They reason from expected dipole moments that the configuration must be



with the Ni atom in the plane of the base. In such a structure the dipole moment should be only that of the Ni-Br bond "for which a value of 2.5D seems very plausible".

Since the compound is formed by the addition of bromine to $\text{NiBr}_2(\text{Et}_3\text{P})_2$ which has a trans-planar configuration, a square pyramidal structure might be expected. This structure is also in accord with Kimball's predictions for d^2sp^3 bonding. However the valence configuration may be dsp^3 for which the trigonal bipyramid is predicted.

Although Lord et al. have shown that the IF_5 molecule is a square pyramid, they apparently were unable to determine the exact position of the iodine atom along the fourfold axis normal to the square base. A dipole moment determination should clarify this question since the existence of a permanent dipole would indicate that the iodine atom is in or near the base whereas a zero dipole moment would indicate a central position above the base.

The proposed structure of $\text{NiBr}_3(\text{Et}_3\text{P})_2$ is open to some doubt. Although the structures of some coordination compounds have been assigned on the basis of dipole moment measurements, these are usually cases in which only two configurations are possible, one with a permanent dipole and the other with zero dipole moment. In the case of $\text{NiBr}_3(\text{Et}_3\text{P})_2$, the structure was chosen by comparison of the observed dipole moment with the predicted dipole moments for the several possible configurations. A structure determined by such a qualitative approach is obviously subject to a much greater possible error than a structure determined by a more direct method such as interpretation of electron diffraction or vibrational spectra measurements.

References:

- (1) G. E. Kimball, J. Chem. Phys., 8, 188-98 (1940)
- (2) L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc., 60, 1836-46 (1938)
- (3) R. V. G. Ewens and W. M. Lister, Trans. Faraday Soc., 35, 681-91 (1939)
- (4) L. Pauling, "Nature of the Chemical Bond", Cornell University Press, Ithica, N. Y., 2nd ed., 1948, p. 110
- (5) N. V. Sidgwick and H. M. Powell, Proc. Roy. Soc. (London) A176, 153-80 (1940)
- (6) A. F. Wells, "Structural Inorganic Chemistry", Oxford University Press, London, 1945, pp. 271, 512
- (7) H. Braune and P. Pinnow, Z. physik. Chem., B35, 239-55 (1937)
- (8) M. T. Rogers, A. L. Wahrhaftig, and V. Schomaker, Abstracts, Atlantic City meeting, American Chemical Society, April, 1947
- (9) R. C. Lord, M.A. Lynch, Jr., W. C. Schumb, and E. J. Slowinski, Jr. J. Am. Chem. Soc., 72, 522-7 (1950)
- (10) K. A. Jensen and B. Nygaard, Acta Chem. Scand., 3, 474-80 (1949)

Bond Lengths in Some Inorganic Molecules

George Speranza

March 21, 1950

Introduction. Most bonds are now regarded as having varying degrees of ionic character. The valence-bond treatment, in terms of resonance between a number of structures differing in distribution of bonding electrons has been adopted as one practical way of overcoming the difficulty of representing such structures. Evidence for resonance comes largely from interatomic distances supported in some cases by physical properties, such as, dipole moments and thermochemical data. At the present time a discussion of bond lengths is essentially a discussion of covalent radii and electronegativity coefficients. It was first assumed that such covalent radii could be assigned to atoms, and that the sums of these radii were equal to the lengths of bonds between pairs of atoms. Departure from the additivity rule indicated that the bonds concerned were not simple electron-pair bonds with equal sharing of electrons. Since the discrepancies were worse for bonds involving the most electronegative elements, Shomaker and Stevenson (3) suggest the equation: $R_{ab} = R_a + R_b - 0.09(X_a - X_b)$ where R_{ab} is the length of bond a-b and R_a and R_b are the radii of covalent a and b. X_a and X_b are the Pauling electronegativity values (1) for a and b.

M-C, MCl_n and MF_n Bonds. The distance for M-C bonds in all cases except M-C, O-C and C-F are to within the experimental error identical with $R_m + R_c$. The introduction of an electronegativity correction to account for these three shorter bond lengths leads to discrepancies of 0.07 Å in Ge-C and Sn-C for which no correction is required (4). Pauling observed that MF_n is often shorter than $R_m + R_f$. On the basis of this shortening he argued that bonds in these halides have some double bond character. Resonance with structures of the type $F_2C = F^+ F^-$ avoids the difficulty about the octet. The length of a particular bond A-B depend also on the nature of the substituents attached to A and B.

| <u>Compound</u> | <u>C-F Bond Length-Å</u> | <u>$R_c + R_f$</u> | <u>S-S Equation</u> |
|--------------------|--------------------------|-------------------------------|---------------------|
| CF ₄ | 1.36 | 1.49 | 1.36 |
| CH ₃ F | 1.42 | 1.49 | 1.36 |
| CCl ₃ F | 1.44 | 1.49 | 1.36 |

The bond lengths in SiF₄, PF₃ and AsF₃ are shorter than that calculated by the Shomaker-Stevenson equation.

Coordinate Covalent Bond. Phillips, Hunter and Sutton (2) have indicated that (CH₃)₃N-O and (CH₃)₂O-BF₃ must be true co-ordinate links because of the octet rule. The lengths of N→O and O→B are nearly equal to those expected for normal single covalent bonds. These investigators showed the S-O bond to be much smaller than the value expected for a single bond. They concluded therefore that the S-O bond is a double bond (S=O) with a small dipole moment. According to Wells this evidence is not conclusive. The degree of asymmetry of sharing the two electrons is not similar in all co-ordinate links, e.g. the charge distribution in S→O need not be the same as in N→O and polarity is not a true measure of coordinate links. It simply indicates that X in $S \xrightarrow{+x} O^{-x}$ is less than y in $N \xrightarrow{+y} O^{-y}$.

The following table shows the results of the investigation of the effect of the various factors on the rate of the reaction. The results are given in the form of a table, the columns of which are headed by the names of the factors investigated, and the rows by the names of the reactions. The numbers in the cells of the table represent the rate of the reaction, expressed in terms of the percentage of the reaction which has taken place in a given time. The results show that the rate of the reaction is affected by the concentration of the reactants, the temperature, and the presence of a catalyst. The rate of the reaction increases with the concentration of the reactants, with the temperature, and with the presence of a catalyst.

The following table shows the results of the investigation of the effect of the various factors on the rate of the reaction. The results are given in the form of a table, the columns of which are headed by the names of the factors investigated, and the rows by the names of the reactions. The numbers in the cells of the table represent the rate of the reaction, expressed in terms of the percentage of the reaction which has taken place in a given time. The results show that the rate of the reaction is affected by the concentration of the reactants, the temperature, and the presence of a catalyst. The rate of the reaction increases with the concentration of the reactants, with the temperature, and with the presence of a catalyst.

| Reaction | Concentration | Temperature | Catalyst |
|----------|---------------|-------------|----------|
| 1 | 1.0 | 25.0 | 0.0 |
| 2 | 1.5 | 30.0 | 0.0 |
| 3 | 2.0 | 35.0 | 0.0 |
| 4 | 1.0 | 25.0 | 0.5 |
| 5 | 1.5 | 30.0 | 0.5 |
| 6 | 2.0 | 35.0 | 0.5 |

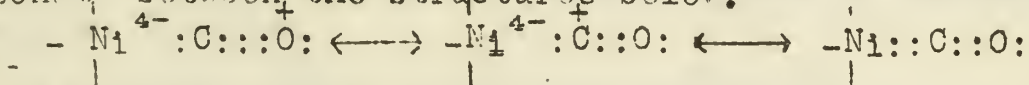
The following table shows the results of the investigation of the effect of the various factors on the rate of the reaction. The results are given in the form of a table, the columns of which are headed by the names of the factors investigated, and the rows by the names of the reactions. The numbers in the cells of the table represent the rate of the reaction, expressed in terms of the percentage of the reaction which has taken place in a given time. The results show that the rate of the reaction is affected by the concentration of the reactants, the temperature, and the presence of a catalyst. The rate of the reaction increases with the concentration of the reactants, with the temperature, and with the presence of a catalyst.

The following table shows the results of the investigation of the effect of the various factors on the rate of the reaction. The results are given in the form of a table, the columns of which are headed by the names of the factors investigated, and the rows by the names of the reactions. The numbers in the cells of the table represent the rate of the reaction, expressed in terms of the percentage of the reaction which has taken place in a given time. The results show that the rate of the reaction is affected by the concentration of the reactants, the temperature, and the presence of a catalyst. The rate of the reaction increases with the concentration of the reactants, with the temperature, and with the presence of a catalyst.

Oxy-Ions. The formulation of the tetrahedral ions with single bonds (Co-ordinate links) has been rejected on the grounds that their lengths are far less than those of single bonds. Sutton claims the non-existence of fluorine oxy-acids because the valency group of fluorine is limited to the octet which is not necessarily so for chlorine in ClO_4^- . Wells suggests that the reason fluorine does not form oxy-ions is because it is the only element which is more electro-negative than oxygen. This would imply that fluorine would be the positive end of a polar bond.

The following points are noteworthy in connection with the conventional resonance formula for oxy-ions and oxy-molecules. 1) The radius of $-\text{O}-$ is the same as that of $-\text{O}-$. 2) The types of resonance postulated is often not consistent with observed bond lengths. For example the S-O bond lengths are the same in SO_2 , SO_3 and probably in SO_4^{2-} . 3) Resonance is not sufficient to account for the shortness of oxy bonds. Pyro-ions of the type $\text{O}_3\text{M}-\text{O}-\text{MO}_3$ would be desirable to study in order to determine the lengths of M-O, M-O-M and the angle between M-O-M.

Metallic Carbonyls and Cyanides. The assumption is made that carbon and not oxygen is attached to metal in carbonyls. The short distance of 1.15\AA for the C-O distance indicates some triple bond character. By using unshared 3d electrons of Ni to form a double bond with carbon the $\text{Ni}=\text{C}$ distance was calculated by Pauling to be 1.79\AA . The observed distance is 1.82\AA . The nickel carbonyl molecule then is said to resonate between the structures below.



The Ni-C distance in complex cyanonickelates have been found to lie in the range $1.85-1.95\text{\AA}$ and although not very accurately known, they appear to be comparable with the value in nickel carbonyl.

References.

1. Pauling, Nature of the Chemical Bond, Cornell University Press, Ithaca, New York, 1942.
2. Phillips, Hunter and Sutton, J. Chem. Soc., 146, (1945).
3. Shomaker and Stevenson, J. Am. Chem. Soc., 63, 37 (1941).
4. Wells, J. Chem. Soc., 55, (1949).

Organogermanium Compounds

Robert F. Vance

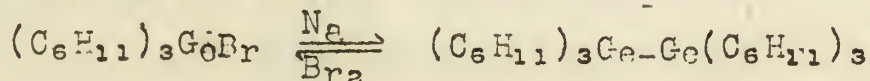
March 21, 1950

Introduction. Within recent months a considerable amount of work has been carried out on the preparation of organogermanium compounds, particularly the halides. As is to be expected, the chemistry of these compounds is quite similar to that of the corresponding silicon compounds. The starting material for most of the organogermanium compounds is germanium tetrahalide. Although easily hydrolyzed, the tetrahalide may be prepared from germanium dioxide and the constant boiling halogen acid by sweeping it from the reaction area with excess hydrogen halide.

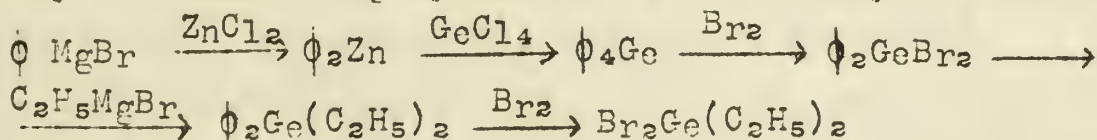
Tetrasubstituted Germanium Compounds. Tetrasubstituted germanium compounds, like those of silicon, may be prepared by Grignard or Wurtz reactions or with zinc, lithium, or mercury alkyls (6,8,9).



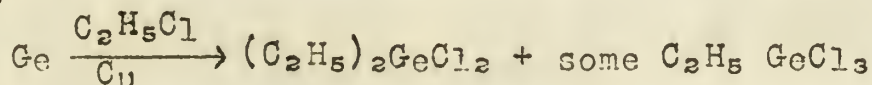
Organolithium compounds have been found to be superior to the corresponding sodium compounds or the Grignard reagent for the introduction of aryl groups (7). A maximum of three cyclohexyl groups can be introduced into the germanium tetrabromide molecule because of their large size. However a smaller alkyl or phenyl group can replace the last bromine atom. Coupling results from the action of sodium on a trisubstituted germanium halide (6). The reaction is reversed by addition of free halogen.



Organogermanium Halides. In most cases these halides are best prepared by similar methods, using smaller quantities of the organic reactant. This procedure always leads to mixtures, but the difference in boiling points is sufficient for separation by fractional distillation. The C-Ge bonds in all these compounds are relatively weak. They are not hydrolyzed at room temperature as are the halides, but the tetraalkyl germanes may be converted to monohalides by addition of halogen (8). The C-Ge bonds from aromatic substituents are weaker than those from aliphatic substituents. This is illustrated by an interesting synthesis of the dialkyl dihalides (10).



This reaction is seldom used since a direct method was developed by Fochow (9).

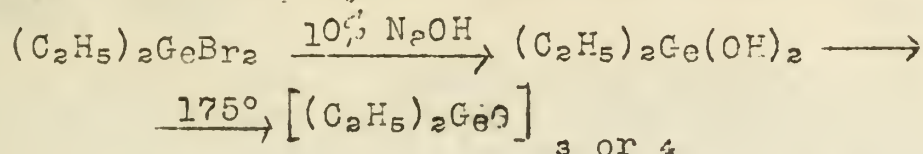


Finely divided silver is a better catalyst for introduction of aryl groups.

Pseudohalides. Although all the isocyanates and isothiocyanates of silicon can be prepared by reaction of silicon tetrachloride with silver isocyanate (AgNCO) or isothiocyanate (AgNCS), the tetraiso-cyanate of germanium has not been obtained in this way (1). However the other isocyanates and all the isothiocyanates are easily prepared.

No explanation of this anomalous behavior has been advanced. Analysis of the silicon series has verified the structure as the iso form, since on hydrolysis isocyanic acid (HNCO) is generated while the cyanate forms ammonium bicarbonate (5).

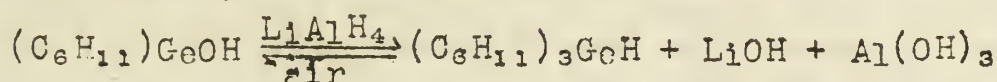
Oxides and Hydroxides. Mono- and dihalides are easily hydrolyzed to the hydroxides by dilute alkali (7). These hydroxides are used in the preparation of polymers much like silicones.



Linear and cyclic tetramers have both been reported. The oxide may be converted to sulfate by refluxing in concentrated sulfuric acid. (2).

Methyl germanium triiodide is solvolyzed by hydrogen peroxide to give a compound of empirical formula $CH_3GeO_{1.5}$. When diluted, CH_3GeOOH , an analog of acetic acid, is obtained (4). Alkoxy derivatives are prepared by treatment of the halide or pseudohalide with an alkoxide (1,7).

Hydrides. Two methods are employed for the preparation of hydrides. Flood proposed treatment of a hexa-alkyl digermene with lithium in liquid ammonia, forming the lithium salt, and subsequent evaporation (8). Lithium aluminum hydride will reduce a halide or hydroxide all the way to the hydride (7).



Conclusion. Reactions of organosilicon compounds have, with relatively few exceptions, been extended to germanium compounds. It would be interesting to attempt the stepwise fluorination of some organogermanium halides by the Swartz reaction ($SbF_3 + SbCl_5$), such as was carried out by Spessard on some silicon compounds (3). Almost no work has been done thus far on the effect of various substituents, such as H, SH, NH_2 , CN, etc., on the organic group.

References

1. Anderson, H.H., J. Am. Chem. Soc. 71, 1799 (1949).
2. Anderson, H.H., *ibid.* 72, 194 (1950).
3. Booth, H.S. and Spessard, D.R., *ibid.* 68, 2660 (1946).
4. Flood, E.A., et al, "Inorganic Syntheses," 1950, Vol. 3.
5. Forbes, G.S., and Anderson, H.H., J. Am. Chem. Soc. 65, 2271 (1943).
6. Johnson, O.H. and Nebergall, W.H., *ibid.* 70, 1706 (1948).
7. Johnson, O.H. and Nebergall, W.H., *ibid.* 71, 1720 (1949).
8. Kraus, C.A. and Flood, E.A., *ibid.* 64, 1635 (1932).
9. Rochow, E.G., *ibid.* 69, 1729 (1947).
10. Trautman, C.E. and Ambrose, H.A., U. S. Pat. 2,416,360; C.A. 42, 2760 (1948).

1. The first part of the report deals with the general situation of the country and the progress of the work during the year.

2. The second part of the report deals with the results of the work done during the year.

3. The third part of the report deals with the financial statement of the year.

4. The fourth part of the report deals with the general remarks of the committee.

5. The fifth part of the report deals with the conclusions of the committee.

6. The sixth part of the report deals with the recommendations of the committee.

7. The seventh part of the report deals with the signature of the committee.

8. The eighth part of the report deals with the date of the report.

9. The ninth part of the report deals with the name of the committee.

10. The tenth part of the report deals with the name of the members of the committee.

11. The eleventh part of the report deals with the name of the secretary of the committee.

12. The twelfth part of the report deals with the name of the treasurer of the committee.

13. The thirteenth part of the report deals with the name of the members of the committee.

14. The fourteenth part of the report deals with the name of the members of the committee.

CRYSTAL GROWTH

February 21, 1950

The following reports are based on papers presented at a Symposium on "Crystal Growth" sponsored by the Faraday Society at the University of Bristol, England, in April, 1949, and published in the Discussions of the Faraday Society, No. 5, (1949).

I. GENERAL THEORY

Alan L. McClelland

The early concept, developed by Ostwald, of a metastable region on the phase diagram in which no crystallization can occur in a system until a certain degree of supersaturation has been reached has been somewhat modified by mathematical treatment of the probability of local concentration fluctuations. Dunning (1) has outlined the derivation of these equations for the rate of nucleation, and shows the dependence of the rate of nucleation on the degree of supersaturation, temperature, crystal density, molecular weight, and interfacial free energy for crystallization of a solid from solution. Experimental verification of the theoretical equations is not complete, but qualitative agreement is indicated.

Theories covering various possible mechanisms of crystal growth are still incomplete, but the papers of Garner (2), Burton and Cabrera (3), and Frank (4) present important evidence on the subject. The three main growth mechanisms postulated are:

(a) The Repeatable Step Process: The relative energies involved in removing ions or molecules from various positions of certain representative crystals have been calculated, and the greatest energy has been found to be that required for removal from an edge. Therefore the greatest tendency toward growth will be at an incomplete edge. Burton and Cabrera (3) have shown that any high order plane will have a terraced structure, and that the terraces will not be regular, but will have irregularities and kinks, and so can grow rapidly by the repeatable step process. Low order planes will be regular and smooth below a certain critical temperature, the actual value of which depends on the crystal system and the plane indices, but above that temperature they will develop surface irregularities and so be able to grow by a process similar to the repeatable step process at an edge.

(b) Surface Nucleation: On a low order plane below the critical temperature mentioned above, growth can occur only by the formation of a new crystal nucleus on the plane surface. This is a relatively slow process compared to the repeatable step process. A high degree of supersaturation is required to force surface nucleation to proceed at a rapid rate.

(c) Growth From Discontinuities: Frank (4) presents arguments in favor of a growth mechanism based on a spiral growth from surface cracks and imperfections. This is essentially the same as growth by the repeatable step process except that the edges are provided by crystal imperfections. Spiral growth is postulated because it accounts for the rapid rate of crystal growth actually observed in many systems at low supersaturations, since growth along a spiral never completes a face, allowing repeatable step growth to proceed continuously without any new surface nucleation.

1. W. J. Dunning, Discussions of the Faraday Society, No. 5. 79-83 (1949).
2. W. E. Garner, *Ibid.*, No. 5, 7-10 (1949).
3. W. K. Burton, N. Cabrera, *Ibid.*, No. 5, 33-48 (1949).
4. F. C. Frank, *Ibid.*, No. 5, 48-54 (1949).

II. Layer Formation on Crystal Faces

Dale E. Jackson

The authors hoped to treat the relation of crystal growth to concentration and surface forces by developing simple physico-chemical expressions. This soon appeared impossible so the work became qualitative, and layer formation was studied by observing the behavior of many different substances.

Certain observations tended to show that material is deposited on faces in successive layers. This was explained by pointing out the greater energy gain by completing an old layer than starting a new one. By observing the interference colors layers a few molecules thick had been followed across the thin, plate-like crystals, of m-toluidine. Similar phenomena had been reported for PbI_2 precipitated from $Pb(NO_3)_2$ and KI.

The microscope was used to observe the growth of layers as they moved across the face of a crystal, formed from a drop of warm, saturated solution. The following generalizations may be made:

1. Layers start from the centers of faces, spreading outward toward the edges.
2. Layer thickness increases as the layers approach the edges of the crystal faces.
3. Layer boundaries are irregular, especially with rapid growth, and their shape conforms to the symmetry of the face.
4. Solute impurities may strongly influence the thickness and shape of the layers.
5. Thick layers have been observed only on faces of certain ionic crystals, not on non-polar materials.

The layers of NaCl vary from 1700-4100Å (600 to 1400 atoms) in thickness and form roughly at a rate of about 0.2mm./min. Certain ionic impurities caused the layers to become variously thicker, thinner or more regular in shape. KH_2PO_4 , $Pb(NO_3)_2$, CdI_2 , were among the other salts which proved feasible for study.

Explanations were offered a) for the information of a few thick layers from many thin ones, b) why organic compounds do not show layer formation, and c) why the layers start at the centers of the faces.

Reference ..

Bunn, C. C. and Emmett, H., Disc. Far. Soc., No. 5, 119-32 (1949).

III. HIGH TEMPERATURE CRYSTAL GROWTH

Paul H. Mohr

High temperature crystal growth has become an important research field in recent years. Probably the greatest impetus in such researches has been the demand for perfect single crystals of many minerals for instrumental and industrial purposes. The natural supply of these materials is not sufficient to meet this demand.

There are several general methods, with many variations, for synthesizing mineral crystals (1). The most convenient method for single crystal growth at higher temperatures is effected by moving a crystal seed in a mineralic melt through a fixed temperature gradient. This method is usually limited to temperatures below 1700°C since materials of construction for use with melts at higher temperatures are lacking. The Verneuil technique (2) for growth of single crystals of refractory materials at extremely high temperatures has recently become popular. There are few published details on successful growth by this means. Briefly, the technique consists of fusing the refractory materials by passing them in a finely divided state through an oxy-hydrogen flame onto a refractory rod. By the proper manipulation, which is largely an art rather than a science, single crystal growth can be induced. The method was first used to grow single crystals of corundum (sapphire) and spinel. Modifications whereby small amounts of other oxides were added to the powder produced colored crystals (rubies). Recently, however, single crystals of rutile (3) and scheelite (4,5) have been grown by this technique.

There are some mineral species which do not adapt themselves well to the melt techniques. These may be synthesized, usually as a last resort, by hydrothermal methods. This involves crystal growth at elevated temperatures and pressures in the presence of water. Although many theoretical and experimental difficulties are encountered in this procedure, considerable effort has been expended to achieve the growth of single crystals of pure quartz. This approach merits considerable attention, since many mineralogists and petrographers believe that water plays an important role in the genesis of minerals.

During World War II an acute shortage of perfect quartz crystals for piezoelectric purposes initiated considerable research. In England the most popular method for synthesizing quartz crystals was an isothermal one using a quartz seed suspended in a melt of sodium metasilicate containing a mineralizer (KHF_2) (6). Silica glass was used to replace the quartz crystallizing from the melt, and growth depended on the much higher solubility of the silica in the vitreous than in the crystalline form. The action of the mineralizer is not well understood, but it is known that alkali silico fluorides are formed. In this country (7) crystalline quartz is used in place of the vitreous silica, and the seed is maintained at a temperature slightly below that of the surrounding region.

1. Zerfoss, Johnson, and Egli, Discussions Faraday Soc., No. 5, 166 (1949).
2. Verneuil, Compt. rend., 135, 791 (1902); Ann. chim. Phys., 3, 20 (1904).
3. Titanium Division, National Lead Co., Sci. Newsletter, Oct. (1947).
4. Linde Air Products Corp., Chem. Eng. News, 27, 48 (1949).
5. Zerfoss, Johnson, and Imber, Physic. Rev., 75, 320 (1949).
6. Thomas, Wooster, and Wooster, Discussions Faraday Soc., No. 5, 341 (1949).
7. Hale, Science, 107, 393 (1948).

IV. CRYSTAL HABIT MODIFICATION AS A MEANS OF REDUCING CAKING OF SALTS. R. Keith Osterheld

The caking of a water soluble salt is a recrystallization process. The first step is the formation of a thin film of saturated solution on the surface of the salt granules. Capillary forces concentrate this film at the points of contact between adjacent granules to form liquid bridges. Subsequent dehydration or temperature variation causes the crystallization of these bridges and the entire bulk of material sets into a solid "cake." It has been common industrial procedure to modify the habit of crystalline substances to improve their handling properties. It has now been shown by Whetstone (1) that crystal habit modification can be used to reduce the caking properties of certain salts.

In an investigation (2) of the effect of dyes upon the crystal habit of ammonium nitrate IV (the form stable from -18° to 32°C) it was noted that Acid Magenta causes a change from the usual needle-like prisms to plates or scales. A 0.03% coating of this dye on ammonium nitrate was observed to greatly reduce its setting tendency. A correlation was then sought between degree of habit modification and reduction in caking for a number of dyes. The degree of modification of ammonium nitrate crystals, produced from solutions saturated with respect to both ammonium nitrate and dye being investigated, was noted. The effect upon caking of a 0.10% coating of the dye was observed. Acid Magenta gave the most marked effect in both cases. Other dyes capable of forcing ammonium nitrate to crystallize in thin plates also gave a marked reduction in caking. Dyes which caused crystallization in the form of prisms or laths had a smaller effect on setting, an effect almost as small as that produced by dyes causing no habit modification. The improvement of setting properties from a dye coating appeared to be related to the crystal habit modification produced by the dye.

The validity of this concept was tested by similar investigations with ammonium sulfate, potassium nitrate, and sodium nitrate. For both ammonium sulfate and potassium nitrate, the dyes causing the most extreme habit changes gave the most marked reduction in setting tendency. Since no dye effectively reduced the caking of sodium nitrate, it is noteworthy that no dye has been found to greatly modify the crystal habit of sodium nitrate.

It was not possible to examine the crystal structure of the solid bridges which are produced in the caking process. However, each of the dyes effective against caking has the property of causing precipitation of crystals of extreme thinness and fragility. Ammonium nitrate crystals produced in the presence of Acid Magenta are very soft when wet and easily broken up when dry. Ammonium sulfate crystals formed in the presence of Amaranth or Tartrazine are very flexible when wet and extremely fragile when dry. This indicates that the effect of the dyes in reducing setting must be connected with their tendency to produce thin, fragile crystals in the intergranular bridges and must be due to a reduction in the mechanical strength of the intergranular bonding as a result of its modified structure.

1. J. Whetstone, Discussions of the Faraday Society, No. 5, 261 (1949).
2. A. Butchart and J. Whetstone, Disc. Far. Soc., No. 5, 254 (1949).

The theories of crystal structure, photochemistry, and radiation chemistry are closely allied. Thus, the study of the effects of radiations on crystals can give information as to their structure.

Causes: The causes of radiation effects are either electromagnetic radiations (gamma rays, X-rays, light) or massive particles (electrons, protons, alphas, neutrons, and fission fragments).

Micro Radiation Effects: The electromagnetic radiations can cause excitation of atoms (including formation of free electrons) and ionization. The term "Photochemistry" refers to photon induced processes in which only excitation occurs². Mott and Gurney explain the action of light on alkali halides and silver halides as being due to the production of a free electron from the halide ion, which electron then migrates through the crystal until it falls into a lattice vacancy or into a crack or crystal disturbance³.

The massive particles moving through matter can lose their energy in three ways: excitation, ionization (production of ion-pairs) and elastic collisions. The electron loses its energy through the first two of these, being of low mass, while the neutron, being uncharged, loses its energy solely through collisions, of which it has a large number.

In elastic collisions the energy transferred many produce either of two effects. Atoms may be ejected from their normal lattice positions to interstitial positions as a result of an energetic impact; or, if the energy transferred is not sufficient to cause a dislocation of the knocked-on atom, lattice vibrations result which degenerate into thermal energy. Approximately 25 eV are required to eject an atom from its lattice position, and it is calculated that about half of the energy lost through elastic collisions produces dislocations.

In beryllium, graphite and aluminum, a 5 MeV alpha particle causes about 33, 54 and 59 dislocations respectively; a 20 MeV proton causes 56, 72 and 79 dislocations; a 2 MeV neutron causes 454, 1870, and 6030 dislocations. A pair of fission fragments with a total of 160 MeV energy are calculated to cause 8300 dislocations if imbedded in graphite and 25,000 in metallic uranium.

Macro Radiation Effects: In those cases where electromagnetic radiations and massive particles produce similar effects (e.g. ZnS phosphors) the effects are thought to be due to electronic excitation and not to dislocations. Whereas electromagnetic radiations are highly selective in producing interactions, the effects of massive particle penetration can be almost always observed. Glasses become colored and fluorescent when exposed to the rays from radium⁴. Pyrex glass turns brown and soft glass purple. White barium salts which contain radium become brown. Diamond is colored green by alphas, but not by electromagnetic radiations or betas. The resistivity, heat conductivity and elasticity of graphite change markedly upon neutron bombardment. Neutrons were observed also to cause an ordered lattice of Cu₃Au alloy to become disordered.

1. F. Seitz, Discussions of the Faraday Soc., No. 5, 271-82 (1949).
2. M. Burton, J. Phys. Chem., 51, 611-26 (1947).
3. Rollefson and Burton, Photochemistry, Prentice Hall (1939).
4. S. Lind, The Chem. Effects of Alpha Part. and Electrons (1928).

The University of Chicago is a leading center of research and scholarship in the fields of the natural and social sciences, the humanities, and the arts. It is a place where the best minds from around the world come to study and work together.

The University of Chicago is a place where the best minds from around the world come to study and work together. It is a place where the best minds from around the world come to study and work together.

The University of Chicago is a place where the best minds from around the world come to study and work together. It is a place where the best minds from around the world come to study and work together.

The University of Chicago is a place where the best minds from around the world come to study and work together. It is a place where the best minds from around the world come to study and work together.

The University of Chicago is a place where the best minds from around the world come to study and work together. It is a place where the best minds from around the world come to study and work together.

The University of Chicago is a place where the best minds from around the world come to study and work together. It is a place where the best minds from around the world come to study and work together.

The University of Chicago is a place where the best minds from around the world come to study and work together. It is a place where the best minds from around the world come to study and work together.

The University of Chicago is a place where the best minds from around the world come to study and work together. It is a place where the best minds from around the world come to study and work together.

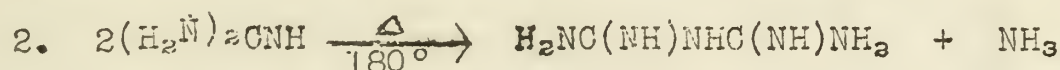
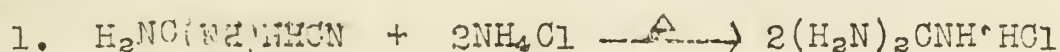
METALLIC COMPLEXES OF BIGUANIDE AND ITS DERIVATIVES

J. R. Kuebler, Jr.

March 28, 1950

INTRODUCTION: While complex compounds of copper, cobalt and nickel with biguanide have long been known, investigators have disagreed concerning their structures (8). With the increased availability of biguanide, Ray and his co-workers have in recent years undertaken a study of the constitution of these complexes with several di- and tri-valent metals.

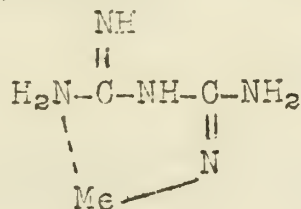
PREPARATION OF THE COMPLEXING AGENTS: Calcium cyanamide, manufactured in commercial quantities by the American Cyanamid Company, is used as the starting material for the preparation of guanidine. CaNCN is made from limestone, coke and nitrogen, and upon treatment with water and carbon dioxide, yields free cyanamide, H_2NCN . The latter is polymerized to dicyandiamide, $\text{H}_2\text{NC}(\text{NH})\text{NHCN}$, which upon fusion with NH_4Cl yields guanidine hydrochloride (equation 1). Biguanide is obtained by the deammonation of guanidine (equation 2).



Substituted biguanides are prepared by the reaction of dicyandiamide and the corresponding amine:



DETERMINATION OF THE CONSTITUTION OF THE COMPLEXES: Ray and Saha (8) selected the structure



(Me = an equivalent of a metal ion)

for the biguanide complexes, from among many other possibilities. These compounds, although saturated inner-metallic complexes can still form salts, due to the presence of the free amino group. The proposed structure is based upon the following observed facts:

1. Neutral, anhydrous tris-(biguanide) chromium (III), $[\text{Cr}(\text{C}_2\text{N}_5\text{H}_5)_3]$ is known (8), indicating that biguanide can function as a bidentate group having one replaceable hydrogen atom.

2. Numerous ionic salts are known (X^- , SO_4^{2-} , OH^- , SCN^- , etc.) having always one equivalent of the anion group per molecule of biguanide in the complex, such as $[\text{Cr}(\text{C}_2\text{N}_5\text{H}_7)_3]\text{Cl}_3$.

3. It has been reported that an imine hydrogen atom may be replaced by a metal ion in amino-guanidine (11), and if such were the case in biguanide, a stable six-membered ring would be formed.

4. The tris-(biguanide)cobalt (III) chloride has been resolved into two optically active isomers (2), indicative of the predicted octahedral configuration.

5. HgCl_2 reacts with tris-(biguanide) cobalt (III) hydroxide, indicating the presence of a free amino group (10).

6. Two forms of bis-(α -naphthylbiguanide) nickel (II) chloride have been observed, which are possibly cis-trans modifications (6).

The following is a list of the names of the members of the American Medical Association who have been elected to the office of President for the year 1928. The names are listed in alphabetical order of their last names.

The following is a list of the names of the members of the American Medical Association who have been elected to the office of Vice-President for the year 1928. The names are listed in alphabetical order of their last names.

The following is a list of the names of the members of the American Medical Association who have been elected to the office of Secretary for the year 1928. The names are listed in alphabetical order of their last names.

The following is a list of the names of the members of the American Medical Association who have been elected to the office of Treasurer for the year 1928. The names are listed in alphabetical order of their last names.

The following is a list of the names of the members of the American Medical Association who have been elected to the office of Editor for the year 1928. The names are listed in alphabetical order of their last names.

The following is a list of the names of the members of the American Medical Association who have been elected to the office of Corresponding Secretary for the year 1928. The names are listed in alphabetical order of their last names.

The following is a list of the names of the members of the American Medical Association who have been elected to the office of Recording Secretary for the year 1928. The names are listed in alphabetical order of their last names.

The following is a list of the names of the members of the American Medical Association who have been elected to the office of Managing Secretary for the year 1928. The names are listed in alphabetical order of their last names.

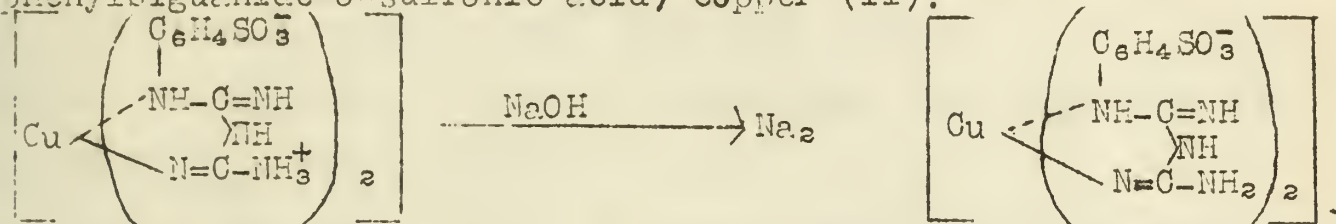
The following is a list of the names of the members of the American Medical Association who have been elected to the office of Executive Secretary for the year 1928. The names are listed in alphabetical order of their last names.

The following is a list of the names of the members of the American Medical Association who have been elected to the office of Assistant Secretary for the year 1928. The names are listed in alphabetical order of their last names.

The following is a list of the names of the members of the American Medical Association who have been elected to the office of Corresponding Secretary for the year 1928. The names are listed in alphabetical order of their last names.

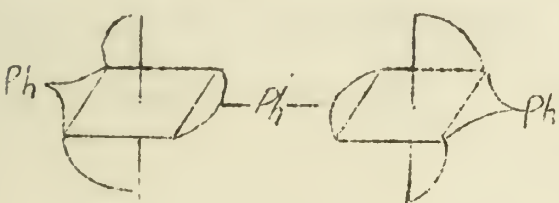
In general, the evidence for the proposed structures was based on chemical analyses, molecular weight determination by the depression of the freezing point, conductometric studies of the number of ions found in solution, and magnetic measurements.

RECENT WORK ON BIGUANIDE COMPLEXES: Ray and Dutt (3) have reported an amphoteric "inner-metallic complex of the fourth order", wherein both the principal valencies and coordination number of the central metallic ion are satisfied, and a separate acidic group capable of forming salts with alkalis is present on the complexing agent. An example is bis-(phenylbiguanide-o-sulfonic acid) copper (II):

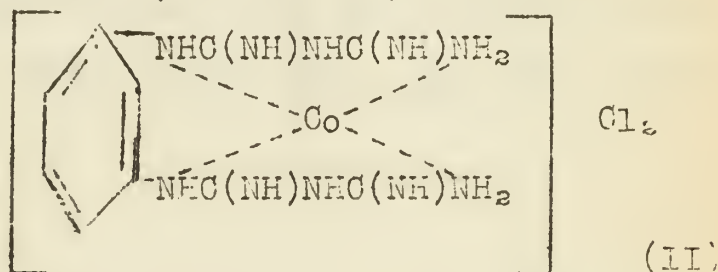


The copper compound has been isolated in two colored modifications; cis-trans isomerism was indicated but the evidence was not conclusive. Only one form of the corresponding cobalt (III) complex has been prepared, although geometrical and stereoisomers might be predicted.

Two types of complexes have been observed with cobalt (III) and chromium (III) and metaphenylenedibiguanide (9). This compound acts as a tetradentate group, forming octahedral complexes with either one molecule of metaphenylenedibiguanide and two other coordinating groups, $[\text{Co}(\text{C}_{10}\text{N}_{10}\text{H}_{16})_2\text{Cl}_2]_3$, or with excess reagent, binuclear, octahedral complexes (I).



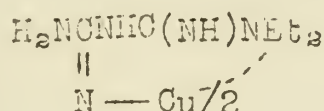
(I)



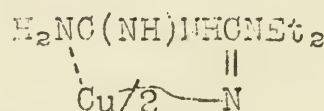
(II)

Cobaltous ion forms a stable compound with this reagent which magnetic measurements indicate may possibly be an associated complex (II) rather than a true inner-metallic complex.

The configuration of bis-(N-diethylbiguanide) copper (II) (5) was studied by the method of Pfeiffer (1), the evidence favoring structure (III) rather than (IV).



(III)



(IV)

Two colored modifications were observed, red and blue; the latter being the most stable was designated as the trans form.

APPLICATIONS: Aside from their academic interest as a new type of complexing agent, biguanide complexes of various metals have proved to be of analytical value. Biguanide sulfate has been used for the gravimetric determination of copper as bis-(biguanide) copper (II) sulfate (7). Tris-(phenylbiguanide) cobalt (III) and tris-(biguanide) chromium (III) cations form precipitates with many complex anions (PtCl_6^{2-} , $\text{Co}(\text{SCN})_6^{3-}$, etc.) which may prove useful for identification or separation (4).

CONCLUSION: Many of the structures proposed by the authors are based on somewhat incomplete evidence, particularly those of the di-valent metals. X-ray crystallographic studies, apparently untried in these cases, could very likely remove a good deal of the uncertainty about the configurations of these biguanide complexes.

BIBLIOGRAPHY

1. Pfeiffer, J: prakt. Chem., 149, 217 (1937).
2. Ray, P. and Dutt, N. K., J. Indian Chem. Soc., 18, 289 (1941)
3. Ibid., 25, 563-70; 589-90 (1948).
4. Ray, P. and Ghosh, N. N., J. Indian Chem. Soc., 15, 347-9 (1938).
5. Ibid., 26, 144-8 (1949).
6. Ray, P. and Ray, H., J. Indian Chem Soc., 21, 163-6 (1944).
7. Ray, P. and Roy-Chowdhury, J., J. Indian Chem. Soc., 18, 149 (1941).
8. Ray, P. and Saha, H., J. Indian Chem. Soc., 14, 670-84 (1937).
9. Ray, P. and Sarma, B. D., J. Indian Chem. Soc., 26, 137-43 (1949).
10. Ray, P. and Siddhanta, S. K., J. Indian Chem. Soc., 18, 299 (1941).
11. Thiele, Ann., 270, 1 (1892).

THE UNIVERSITY OF CHICAGO
DEPARTMENT OF CHEMISTRY
JANUARY 1951

EXPERIMENTAL

1. Preparation of the sample (1951)
2. Measurement of the rate of reaction (1951)
3. Determination of the equilibrium constant (1951)
4. Study of the effect of temperature on the rate of reaction (1951)
5. Study of the effect of concentration on the rate of reaction (1951)
6. Study of the effect of catalyst on the rate of reaction (1951)
7. Study of the effect of solvent on the rate of reaction (1951)
8. Study of the effect of pressure on the rate of reaction (1951)
9. Study of the effect of light on the rate of reaction (1951)
10. Study of the effect of magnetic field on the rate of reaction (1951)

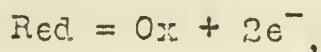
DISPROPORTIONATION IN INORGANIC COMPOUNDS

Gladys H. Quinty

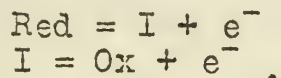
March 28, 1950

The process of disproportionation is one in which similar molecules or ions interact to give products which differ either in the magnitude of the ion charge or in the relative weights of the ionic or molecular products; the former reactions involve electron transfer and the latter, atom transfer. Such reactions occur quite frequently when a compound exists intermediate in valency between two others.

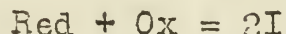
If the simple oxidation of a bivalent metal is considered, it is obvious that if the metal has only one state of valency, the reaction can proceed in only one way. However, if the metal has a fairly stable univalent state as well, the reaction can proceed stepwise with the formation of an intermediate compound. This intermediate compound is, of course, an "ous" salt. Thus, in the general reaction,



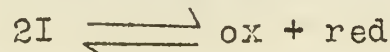
the stepwise process can be represented by the two equations,



If the intermediate is a fairly stable salt,



The reciprocal of the equilibrium constant, then, represents the disproportionation constant for the reaction

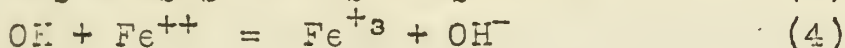
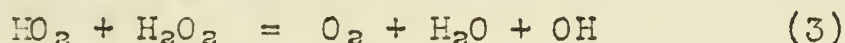
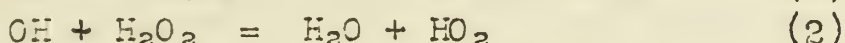
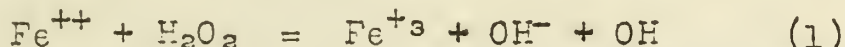


Like all other reactions, the free energies of the compounds concerned must be considered in order to determine whether a disproportionation will proceed. Free energies, however, do not indicate the speed of the reaction. Generally, electron transfer reactions require but a small activation energy and are very rapid, while atom transfer reactions, in which a covalent link is broken, are usually slow. Thus, "cationic" disproportionations reach equilibrium rapidly in contrast to changes such as sulfurous acid to sulfuric acid and free sulfur, or permanganate to the manganous salt. In many such reactions, it is probable that free radicals are involved through stepwise transfer of electrons.

A classic example of a simple disproportionation is that of copper (I) into copper (II) and free copper. Many copper (I) salts decompose instantly on contact with water but those which are very insoluble or strongly complexed are stable.

Essentially, the reaction $\text{Hg}_2^{++} \rightleftharpoons \text{Hg} + \text{Hg}^{++}$ strongly resembles that of the copper. However, the free energy change in the reaction indicates that the lower valence state should be the more stable. Nevertheless, the equilibrium is easily reversed and the stabilities are based upon the relative solubilities of the Mercury (I) and Mercury (II) compounds.

The reactions involving atom transfer are not simple reactions as the equations tend to indicate but occur usually by a series of stepwise processes. It has already been mentioned that, in all probability, free radicals are involved. In order to illustrate the complexity of such a procedure, a specific reaction can be considered in more detail. The decomposition of hydrogen peroxide may be regarded as a disproportionation since the free oxygen is in a different state of oxidation from that of the combined oxygen. Also, it seems probable that if this reaction proceeds by several electron transfers, the addition of a substance which is oxidized readily by such transfers should catalyze the reaction. Thus, the decomposition is catalyzed by iron (II) and copper (I) salts. The effect of iron (II) has been considered by Haber and Weiss and the main stages in the reaction are shown in the following equations:



Equations (2) and (3) represent the chain mechanism and (4) its termination. When the concentration of the iron (II) becomes very small, reaction (4) no longer takes place and new reactions must be proposed to explain the process.

Many of these reactions are of great importance industrially. The entire process of nitric acid manufacture from ammonia depends upon the disproportionation of nitrous acid into nitric acid. The disproportionation of carbon monoxide into carbon and carbon dioxide in the blast furnace is of critical economic importance. Also worth mentioning is the old method for the preparation of permanganates which is based upon the disproportionation of the manganates into permanganate and manganese dioxide.

Many other inorganic disproportionation reactions can be cited but no features are displayed which have not been pointed out already. As would be expected, intermediate compounds of nitrogen, phosphorus, sulfur, the halogens, gold, tin, rhenium, thallium, etc., disproportionate. Of more recent interest is the work of Heyrovsky who has shown by polarographic studies that when zinc is electrolytically reduced, the product first formed is a univalent zinc ion which disproportionates into zinc and the divalent ion.

REFERENCES

- (1) Wilson, H. N. and Bremner, J. G. M., Quart. Rev. 2, [1], 1 (1948)
- (2) Haber, F. and Weiss, J. Proc. Roy. Soc. [A] 147, 332 (1934)
- (3) Heyrovsky, Chem Ztg. 40, 24, (1947)
- (4) Latimer, W. M., Oxidation Potentials, Prentice-Hall Inc., New York, New York, 1938

TITRIMETRY IN NON-AQUEOUS SOLUTIONS

William A. Ziegler

April 4, 1950

INTRODUCTION

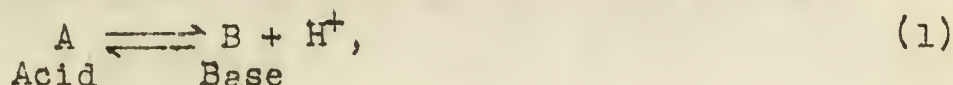
Comparatively little use has been made of non-aqueous systems in volumetric analysis. Non-aqueous solvents would afford the following advantages:

- (1) Differentiation in strength of acids (or of bases), particularly those which have comparative strengths in water.
- (2) Determination of salts of very weak acids by direct acidimetric titration.
- (3) Greater rapidity of determination in some instances²².
- (4) Determination of both acidic and basic groups on the same molecule.

Most of the work in non-aqueous solutions deals with acid-base reactions where use of solvents of different acidic or basic character serves to the greatest advantage.

THE EFFECT OF SOLVENT UPON ACID STRENGTH

Since the value of the dissociation constant of an acid depends partially on the basic strength of the solvent, such a constant is not a proper criterion for judging acid strength in various solvents¹⁰. As proposed by Bronsted, for the equation



we may write

$$K_A = \frac{c_B}{c_A} (a_{H^+}), \quad (2)$$

where K_A is the acidity constant of the acid, (a_{H^+}) denotes the proton activity, and c_A and c_B are, respectively, the "conventional activities" of the acid and the base and are considered equal to the concentrations in very dilute solutions. The basicity constant K_B of the base is the reciprocal of K_A . For the same reaction the activity acidity constant $K_{A, \text{Act.}}$ is given by

$$K_{A, \text{Act.}} = \frac{(a_B)(a_{H^+})}{(a_A)} = \frac{(c_B)(a_{H^+})}{(c_A)} \frac{f_B}{f_A} = K_A \frac{f_B}{f_A}, \quad (3)$$

where f_A and f_B are the activity coefficients of the acid and the base. The activity acidity constant is an absolute thermodynamic constant independent of ionic strength and solvent but is of little value because of our ignorance of the quantitative values of the activity coefficients.

K_A and K_B can be used to compare acidic strengths in different solvents since they are varied by changes in the activities of A and B caused by the dielectric constants of the solvents. In going from a solvent of high dielectric constant to one with a lower value, the increase in f is greater the higher the charge of the ions. A

rearrangement of equation (3) to give

$$K_A = K_A \text{ Act. } \frac{f_A}{f_B} \quad (4)$$

enables us to predict the relative change of acidic strength upon transfer of solvents on the basis of the ions involved in the dissociation of the acid. Such predictions will not hold rigidly, however, if the dielectric constant is less than 20, in which case the strengths of positively charged acids no longer vary, and those of negatively charged acids tend to increase²¹.

Acid dissociation constants involve a reaction with the solvent; for an acid in water this can be shown to be:

$$K_{\text{Diss.}} = \frac{c_B \times c_{\text{H}_3\text{O}^+}}{c_A} \quad (5)$$

A similar relation can be written for other solvents. The acidic or basic properties of a solvent also determine acidic strength. The leveling effect of water causes the strong acids to have comparable strength equivalent to that of the hydronium ion, while in a basic solvent like ammonia, acid strengths will be "leveled down" still farther to that of the ammonium ion. The leveling effect is absent in aprotic solvents i.e., those which either do not contain or do not dissociate hydrogen. The relative strengths of acids and bases per se is developed under such conditions where the solvent has no influence.

END POINT DETERMINATION

The potentiometric method is most generally applicable, if suitable electrodes can be found. Potential readings are relative rather than absolute. Conductometric titrations are also practical in many cases.

Indicator characteristics may vary widely in different solvents because of differences in dielectric constants, differences in solubility, salt errors, and differences in color of the indicator ion or molecule. Although there is at present no certain method of predicting the proper indicator to use, the problem can be attacked in three ways: (1) By drawing a close analogy to the similar titration in water, provided that the indicator is of the same charge type as the weak acid or base being titrated. (2) By observing color changes of various indicators while following the titration potentiometrically to determine the equivalence point. (3) By trial and error, checking the end point obtained against the stoichiometry of the reaction.

CHOICE OF SOLVENTS

For the titration of weak acids such as those found in fats, waxes, and various types of oils the lower alcohols serve as suitable solvents, chiefly because of their solvent properties for these materials. Furthermore, sharper end points may be possible because the ion product constant, of ethanol for example, is much less than the K_w of water. Consequently, a greater range of hydrogen ion concentration exists between an acid and an alkaline solution^{1,10}. Isopropanol¹⁷, *n*-butanol²³, and amyl alcohol¹⁸ are used as substitutes for ethanol if they offer any advantages in solubility for materials like transformer oils or if the indicators used happen to show more distinct colors. Methanol possesses intermediate properties between water and ethanol in reducing ionization constants. Both alcohols

have some base-leveling properties so are also useful in the titration of weak bases although the strong acids used may partially esterify the alcohol. It is even possible to titrate the acid component of salts of fairly strong bases in ethanol¹¹.

Titrations of salts of weak acids and of strong acids in the presence of weak acids without hydrolysis complications are successfully performed in a G-H (Glycol-Hydrocarbon) solvent, which is a mixture of ethylene or some other glycol with a hydrocarbon solvent like chloroform or propanol¹⁵. Such a mixture offers greater solvent power and sharper end points than the alcohols alone. Mixtures of benzene and isopropanol have also been used for similar purposes¹³.

The most satisfactory medium for the titration of weak bases is acetic acid, which is a base-leveling solvent¹⁹. The relative strengths of many acids and bases have been determined in acetic acid^{9,12} and a pseudo-pH scale has been proposed⁷. Perchloric acid is the strongest and most suitable titrant⁸. Sulfuric acid is objectionable because its second ionization is just strong enough to produce peculiar titration curves; hydrochloric and hydrobromic acids are weaker but also too volatile in acetic acid solution. Bases as weak as acetoxime can be titrated in this solvent; for even weaker bases like acetamide or urea use is made of propionic acid which has even greater acid character than acetic²⁰.

For the titration of weak acids an acid-leveling solvent like pyridine is desired⁵. Acids as weak as the enol form of β -dicarbonyl compounds can be determined^{2,3,4,6}. By titrating with standard acetic acid strong bases like sodium hydroxide can be determined in the presence of amines without interference. Monoethanolamine which has similar properties can also be used for the same purposes¹⁶. For weaker acids the more strongly basic ethylenediamine¹⁹ can be used to determine phenols and will even show two distinct breaks in the curve for compounds like resorcinol and salicylic acid¹⁴. The basic solvents, however, all suffer from the same disadvantage in that carbon dioxide and moisture are readily absorbed by basic solutions so that frequent standardizations and carefully-run blanks are always necessary.

BIBLIOGRAPHY

1. Bishop, Edna R., Kettredge, Esther B., and Hildebrand, Joel H., J. Am. Chem. Soc. 44, 135-40 (1922).
2. Carbide and Carbon Chemicals Corp., Works Laboratory Manual, 3-1-250 and 3-1-250.1, January 6, 1949.
3. Ibid., 3-77-4, July 15, 1947.
4. Ibid., 3-166-4a, July 25, 1947.
5. Ibid., 3-734-10, March 9, 1949.
6. Ibid., 3-956-3b, July 25, 1947.
7. Hall, Norris F., and Conant, James B., J. Am. Chem. Soc. 49, 3047-61 (1927).
8. Hall, Norris F., and Werner, Tyrrell H., J. Am. Chem. Soc. 50, 2367-86 (1928).
9. Hantzsch, A., and Langbein, Werner, Z. anorg. allgem. Chem. 204, 193-207 (1934).
10. Kolthoff, I.M., and Rosenblum, Charles, Acid-Base Indicators, Macmillan, New York, 1937.

...the ... of ... in ...
...the ... of ... in ...
...the ... of ... in ...

...the ... of ... in ...
...the ... of ... in ...
...the ... of ... in ...

...the ... of ... in ...
...the ... of ... in ...
...the ... of ... in ...

...the ... of ... in ...
...the ... of ... in ...
...the ... of ... in ...

...

1. ...
2. ...
3. ...
4. ...
5. ...
6. ...
7. ...
8. ...
9. ...
10. ...

11. Kolthoff, I. M., and Stenger, V. A., Volumetric Analysis, Interscience Publishers, Inc., New York, 1947, Vol. II.
12. Kolthoff, I. M., and Willman, A., J. Am. Chem. Soc. 56, 1007-13 (1934).
13. Lykken, L., Porter, P., Fuliffson, H.D., and Tuemmler, F. D., Ind. Eng. Chem., Anal. Ed., 16, 219-34 (1944).
14. Moss, M. L., Elliott, J. H., and Hall, R. T., Anal. Chem. 20, 784-8 (1948).
15. Palit, Santi R., Ind. Eng. Chem., Anal. Ed. 18, 246-51 (1946).
16. Pinkston, John T., and Briscoe, H. T., J. Phys. Chem. 46, 469-73 (1942).
17. Schuette, H. A., and Smith, Maybelle P., Ind. Eng. Chem. 18, 1242 (1926).
18. Seltz, Harry, and McKinney, D. S., Ind. Eng. Chem. 20, 542-4 (1928).
19. Sutherland, W. W., Carbide and Carbon Chemicals Corp., South Charleston 3, W. Va. Private communication to Dr. Jacob Kleinberg, March 23, 1949.
20. Terjesen, Sven G., and Sandved, Karl, Egl. Norske Videnskab. Selskabs. Skrifter, No. 7, 20 pp. (1938); C. A. 33, 4495 (1939).
21. Wolff, J. P., Anal. Chim. Acta 1, 90-112 (1947).
22. Wolff, J. P., Inds. corps gras 1, 36-9 (1945).
23. Wooten, Leland A., and Hammett, Louis P., J. Am. Chem. Soc. 57, 2289-96 (1935).

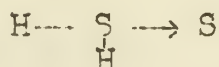
S. W. Pines

April 4, 1950

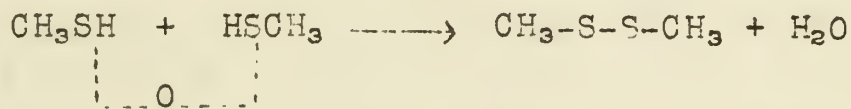
Introduction .

Crude hydrogen "persulfide" has been known for over 150 years. (2) Scheele reported the presence of such an oil in 1777; Thenard assigned a formula of H_2S_2 to it in analogy to hydrogen peroxide, which he had discovered. Later he concluded that the crude oil can best be represented by a mixture of H_2S_x , with x ranging from 2 to 8.

Block and Hohn (9) were able to isolate H_2S_2 and H_2S_3 by distillation. They obtained the higher homologs in an impure form. The structure of H_2S_2 was first depicted in the following manner:



where the "persulfidic" sulfur atom was assumed to be coordinated with the central sulfur atom. This seemed possible by analogy to the polyhalogenides KI_3 , and CH_3ICl_4 (2). The preparation of dimethyl disulfide by oxidation of methylmercaptan also made it appear probable that a chain structure could be assigned to H_2S_2 .



Preparation of the polysulfides.

Most of the polysulfides are prepared in the same manner. A solution of alkali polysulfides is added to concentrated HCl. The crude material that separates in an oily layer contains H_2S_x with x ranging from 2 to 8 or 9, and some free sulfur.

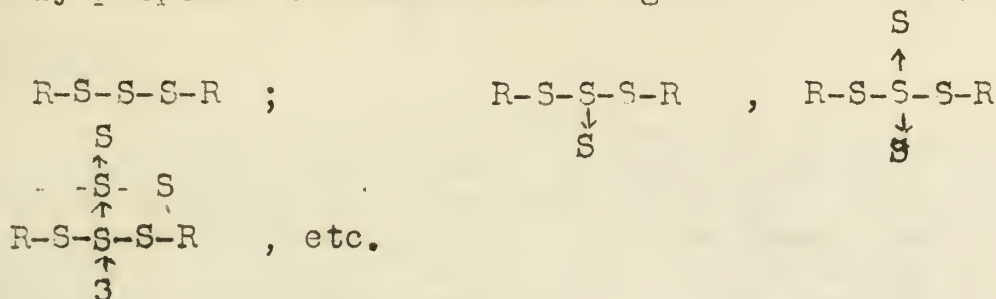
Fractional distillation will give a reasonable yield of H_2S_2 and H_2S_3 . However if these two materials are desired in preference to the other sulfide, Fehér's cracking process (3)(4) can be used for isolation. (see diagram).

H_2S_2 can be obtained from the same mixture by distillation through a special short path still (5). Control of the temperature in the distillation pot and the receivers is essential.

Isolation of H_2S_5 from the oily mixture is difficult. It can be prepared by treatment of ammonium pentasulfide with anhydrous formic acid (7).

H_2S_8 has been obtained from the crude persulfide oil by distillation at 10^{-4} mm Hg (1). It had been isolated previously in the form of complexes with strychnine and brucine (8). It can also be obtained by the solution of sulfur in either H_2S_2 or H_2S_3 . H_2S_8 is unstable in the free state above $-1.45^\circ C$. (8). Finally, a higher sulfide has been prepared electrolytically by the reduction of SO_2 in acid solution (6). Analytical results for this material correspond to the formula $H_2S_{8.5}$. It is considered to be a mixture of H_2S_7 and H_2S_9 . (It could also be regarded as a mixture of H_2S_8 and H_2S_9 .)

The structures of all the sulfides have not been established definitely. H_2S_2 and H_2S_3 are linear; the others are though to be linear molecules by analogy to organic polysulfides. However, recently proposed structures for organic sulfides as



The Raman spectrum (2) of H_2S_2 shows a strong resemblance to H_2O_2 . It is highly probable that

1. The sulfur to sulfur link is a primary valence bond.
2. Cis-trans isomerization can and does occur.

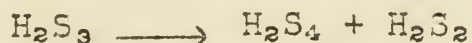


The other sulfides have been characterized by Raman spectra and the values for the predominant frequencies are in the literature. The structures, however, are not completely elucidated. Foss (10) has recently concluded that the higher polysulfides are all linear.

The polysulfides are light yellow oils, resembling olive oil in appearance. No distinct boiling points or melting points are reported. The available data are listed below.

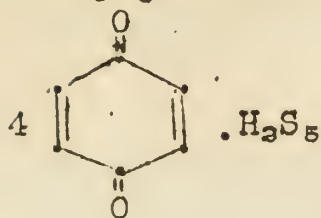
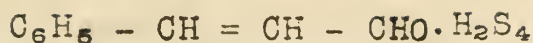
$$\text{H}_2\text{S}_6 \quad d^{15} \quad 1.699$$

The polysulfides decompose at elevated temperatures, or under the influence of base, glass, etc., into H_2S and S . Disproportionation is believed to occur in some cases.



Compounds.

Besides the compounds formed between H_2S_8 with Strychnine and Brucine, some solid derivatives of ketones and aldehydes have been characterized (8), for example,



Conclusion.

The structures of the higher members of the polysulfide series have not yet been established; it would seem that further work in this field may help to solve this question. The problem will probably not be solved chemically because of the great instability of the polysulfides. Perhaps a correlation can be drawn on the basis of further work with these materials and the organic polysulfides, notably those that are formed as byproducts in the manufacture of mustard gas (β , β' dichlorodiethyl sulfide).

Literature Cited

- 1) Fehér, F., and Baudler, M.: Z. anorg. Chem. 258, 132 (1949).
- 2) Z. Elektrochem. 47, 844 (1941).
- 3) Z. anorg. Chem. 254, 251 (1947).
- 4) Z. anorg. Chem. 253, 170 (1947).
- 5) Z. anorg. Chem. 254, 289 (1947).
- 6) Fehér, F., and Feuer, E.: Angew. Chem. A59, 237 (1947).
- 7) Bloch, I., and Höhn, F.: Ber. 41, 1961, 1971, 1975, 1980 (1908).
- 8) Walton, J.H., and Whitford, E.L.: J. Am. Chem. Soc. 45, 601 (1923).
- 9) Mills, H., and Robinson, P.: J. Chem. Soc. 1928, 2326.
- 10) Foss, O.: Kgl. Norske, Videnskab. Selskabs. Forh. 19, No. 20., 72-5 (1946); C.A. 42 53^c (1948).

THE DESIGNATION OF SPECIAL ISOTOPES IN THE NAMES AND FORMULAS OF INORGANIC COMPOUNDS

L. Elmer Olson

April 11, 1950

That elements consist of atoms having different atomic weights was discovered in 1913 by Fajans (1) and by Soddy (1a) as a result of the study of the decay of the radioactive elements which occur in nature. It was found that several varieties of elements could be obtained having different radioactive properties but otherwise chemically identical in every respect. The theory of radioactive disintegration showed that these varieties of atoms must have different atomic weights and this was proved by atomic weight determinations and by the use of the mass spectroph. It is now known (2) that there are over 600 isotopic species which make up the 98 known elements. Most of these are radioactive and have been produced by artificial means.

The recent availability of many pure isotopes and the very rapid expansion of scientific literature relating to work involving special isotopes provides ample evidence for the need for standardization of isotope designation as an integral part of systematic nomenclature.

The isotopes of hydrogen were given separate names corresponding to their mass. This system was not carried on to isotopes of other elements because deuterium was the only readily available isotope (3). To eliminate inconsistencies which show up so readily in such places as the Decennial Index of Chemical Abstracts the Committee on Nomenclature, Spelling and Pronunciation of the American Chemical Society issued a report on the nomenclature of hydrogen isotopes and their compounds (4). The name deuterium proposed by the discoverers for the hydrogen isotope of mass 2 had come into wide use and the committee felt that hydrogen isotopes because of their great difference in mass presented a special case and that the symbols D and T were more convenient than H^2 and H^3 . Deuterium compounds may be named as derivatives of the parent compound or as a compound of the isotope. The system favored by the committee and subsequently adopted by Chemical Abstracts is a modification of a system proposed by Boughton (5).

Examples.

| Compound | Boughton name | Deuterio name |
|------------------------|--|--|
| NH_2D | ammonia-d | deuterioammonia |
| ND_3 | ammonia- d_3 | trideuterioammonia |
| $DHSO_4$ | sulfuric acid-d | sulfuric(mono)deuterioacid |
| $Na_2SO_4 \cdot 5D_2O$ | sodium sulfate penta(hydrate- d_2) | sodium sulfate penta- dideuteriohydrate |
| NH_2D_2OD | ammonium- d_2 hydroxide-d | dideuterioammonium deuterioxide |

The most recent comprehensive system for naming isotopes in inorganic compounds has been proposed by Watt (6) and is set forth in the following rules.

RULE 1. In both formulas and names of inorganic compounds, special isotopes are designated by mass numbers supplemented where necessary by appropriate symbols.

RULE 2. In all symbols and formulas the mass number is written as a right superscript.

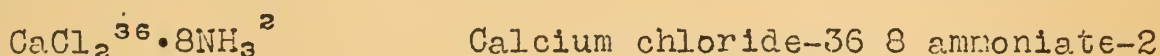
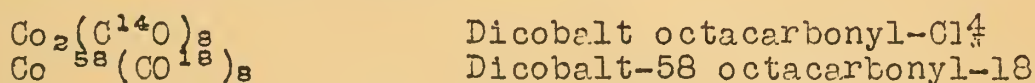
This practice which is common in the United States represents a deviation from the recommendation included in the 1940 report of the International Union of Chemistry (7). Europeans follow the recommendations of the International Union, namely that the mass number be written as a left superscript and that the right superscript position be reserved for its traditional indication of ionic charge or oxidation state.

RULE 3. In the names of inorganic compounds, a special isotope is designated by insertion of the mass number immediately following the appropriate part of the systematic name. The mass number is set apart by a hyphen or hyphens and preceded by the corresponding symbol whenever the compound involves two constituents having overlapping ranges of mass numbers.

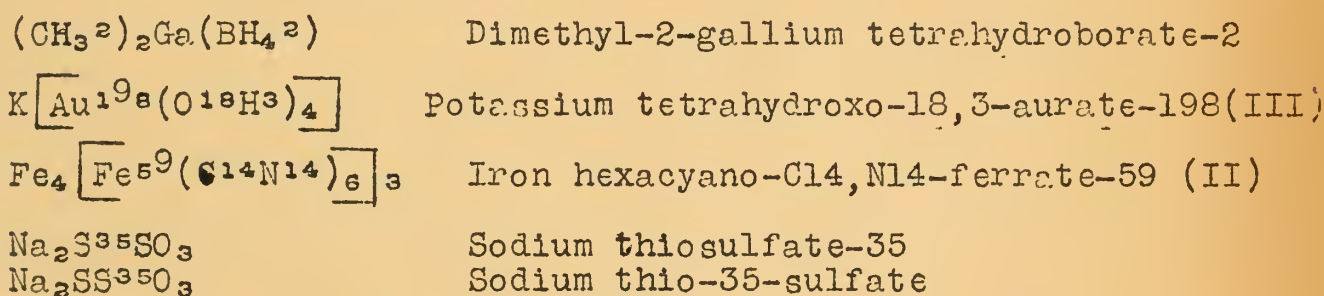
Examples.



Where both the mass number and designation of oxidation state are included, the mass number stands first.

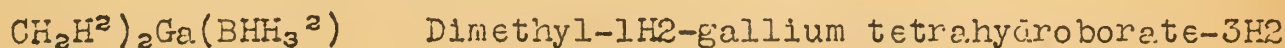


In the last example H^2 is used instead of the symbol D; separate names and symbols are eliminated for special isotopes.



The last two examples represent cases in which exchange experiments have demonstrated a structural difference. To specify the position of the isotope the symbol for sulfur in the formula is repeated while repetition of the mass number in the name appears desirable when the isotope is present in both positions.

RULE 4. Partial substitution by a special isotope is indicated by application of the forgoing rules, inclusion of the appropriate symbol, and insertion of a suitable coefficient specifying the extent of substitution.



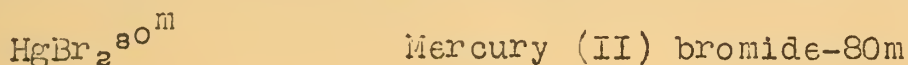
This may become unwieldy when unduly extended but it may prove useful also as a scheme for designation of the percent enrichment with respect to a particular isotope. In "tracer" work the percent of the special isotope may be described in the text as one would give the purity of the reagents used.

RULE 5. Whenever it is necessary to specify both mass number and ionic charge the symbol together with the mass number as a right superscript is inclosed in parenthesis and followed by the usual charge designation.



The need for both rules 2 and 5 would be eliminated if American scientists would adopt the practice of writing mass numbers as a left superscript.

RULE 6. Meta stable nuclear species are denoted by appending the lower case letter m to the mass number.



The suggestions set forth in the forgoing rules will undoubtedly find much favor as a guide to the naming of isotopes in inorganic compounds. Isotopes of hydrogen represent exceptions since special names have had wide usage. The isotopes of hydrogen may not be unique in their physical and chemical differences, but they are unique in that their mass numbers and combining ratios overlap and when given orally lead to confusion unless special names are used to distinguish between the isotopes.

References

- (1) Fajans, Ber., 35, 240 (1913)
- (1a) Soddy, Chem. News., 107, 97 (1913)
- (2) Urey, Science, 108, 489 (1948)
- (3) Otvos and Wagner, Science, 106, 409 (1947)
- (4) Crane, Ind. and Eng. Chem., 13, 200 (1930)
- (5) Boughton, Science, 79, 159, (1934)
- (6) Watt, Science, 108, 740 (1948)
- (7) Jorissen, et. al., J. Am. Chem. Soc. 63, 889 (1941)

STABILIZATION OF UNUSUAL OXIDATION STATES BY FORMATION OF PERIODATES AND TELLURATES

Melvin Tecotzky

-125-

April 11, 1950

Compounds of elements in their higher oxidation states are frequently formed in alkaline medium through the use of an acidic coordinating group. The higher the oxidation state of the central atom in a coordinating group, the more acidic is the group. Periodates with I^{VII} and tellurates with Te^{VI} , are effective in stabilizing higher oxidation states.

Molatesta (1) has prepared salts of trivalent copper, silver, and gold corresponding to the type formula, $M_7^{+}Cu^{III}(IO_6)_2 \cdot nH_2O$ where M represents sodium, potassium, or hydrogen; or a combination of the three. The copper may be replaced by silver or gold. The fact that the gold salt can be made directly from gold (111) lends credence to the trivalency of copper, silver, and gold in this class of compounds. These salts are diamagnetic crystalline substances whose colors vary from brown (copper) to yellow (gold). The stability of these compounds increases from copper to silver to gold.

They are prepared by oxidation with persulfate in a strongly alkaline solution. The copper compounds can be prepared by anodic oxidation. The potassium salts are very soluble and difficult to isolate. The sodium salts are less soluble and are obtained by metathesis from the potassium salt. The sodium salts have not been prepared directly. The following periodates have been prepared:

| Compound | Color |
|---|------------------------|
| $K_7Cu^{III}(IO_6)_2 \cdot 7H_2O$ | emerald green to brown |
| $Na_7Cu^{III}(IO_6)_2 \cdot 12H_2O$ | brown |
| $HK_6Ag^{III}(IO_6)_2 \cdot 10H_2O$ | orange |
| $HK_6Ag^{III}(IO_6)_2 \cdot KOH \cdot 8H_2O$ | orange |
| $HKNa_5Ag^{III}(IO_6)_2$ | yellow orange |
| $KNa_6Ag^{III}(IO_6)_2 \cdot NaOH \cdot H_2O$ | dark yellow |
| $H_2Na_5Au^{III}(IO_6)_2 \cdot 17H_2O$ | yellow |

Copper and silver salts in strongly alkaline tellurate solutions are oxidized with persulfate to compounds containing copper (111) and silver (111). Brauner and Kuzma (2) were, however, unable to isolate the resulting compounds.

Molatesta (1) found the compounds formed by tellurates to be similar to the corresponding periodates. The potassium salts are very soluble and difficult to isolate, whereas the sodium salts are very slightly soluble. Salts such as $H_4Na_5Cu^{III}(TeO_6)_2 \cdot 18H_2O$, $H_3Na_6Ag^{III}(TeO_6)_2 \cdot 18H_2O$, and $H_3Na_6Au^{III}(TeO_6)_2 \cdot 14H_2O$ have been prepared. The sodium salts are quite stable in the solid state. They are easily reduced by contact with organic materials such as alcohol and acetone.

These compounds are prepared in the same way as the periodates using $Cu(OH)_2$, Ag_2O , and H_2AuCl_4 to each of which is added KOH , TeO_2 , $K_2S_2O_8$, and $NaOH$. The copper (111) tellurates are yellow brown, of silver (111) are yellow, and those of gold (111) are almost colorless.

Ray and Sarma (3) undertook subsequently to stabilize higher valent nickel in an analagous manner. Hall (4) had previously reported the preparation of a quadrivalent nickel molybdate. Ray and Sarma treated a solution of nickel sulfate with a solution of sodium periodate. They heated this mixture nearly to boiling and then added sodium persulfate. The light green solution gradually darkened; dark purple to black crystals separated from solution. The crystals were found to correspond in composition to the formula $\text{NaNiIO}_6 \cdot \text{H}_2\text{O}$. This substance is practically insoluble in water and emits an odor of ozone. The potassium compound was prepared in the same manner using potassium persulfate and potassium periodate.

Magnetic measurements have shown that the Cu (III), Ag (III), and Ni (IV) periodate compounds are diamagnetic (1, 3). It has been suggested that the nickel salt is octahedral in structure and should be represented as $\text{Na}[\text{Ni}^{\text{IV}}\text{IO}_6] \cdot \text{H}_2\text{O}$. The copper and silver salts are reported to have a square planar configuration and should be represented as $\text{M}_7[\text{IO}_6 - \text{Cu}^{\text{III}} - \text{IO}_6] \cdot \text{XH}_2\text{O} (3)$.

Methods for preparation of these compounds could be improved possibly by the use of ozone as an oxidizing agent. By using alkali persulfate as the oxidizing agent, the higher valent compounds are contaminated with alkali sulfate.

REFERENCES

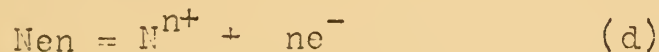
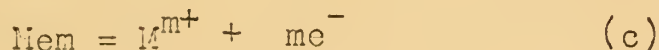
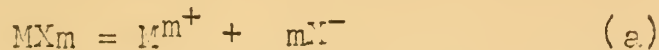
- (1) Malatesta, L., Gazz. Chim. Ital. 71, 467, 580 (1941)
- (2) Brauner, B. and Kuzma, B., Ber. 40, 3369 (1907)
- (3) Ray, P. and Sarma, B., J. Indian Chem. Soc. 25, 205 (1948)
- (4) Hall, R. D., J. Am. Chem. Soc. 29, 692 (1907)

Catalytic Activity of Metals Produced by Reduction in Liquid Ammonia

William W. Campbell

April 18, 1950

I. Introduction: Kraus and Kurtz (1) were the first to propose a mechanism for the reduction of metals in liquid ammonia. If the salt MX_m is reduced by the metal Nn , then the following ionic constituents are involved: M^{m+} , Nn^{n+} , X^- and e^- .



The equilibrium expressions may be represented as follows:

$$\frac{[M^{m+}][X^-]^m}{[MX_m]} = K_1 \quad (1)$$

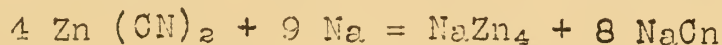
$$\frac{[N^{n+}][X^-]^n}{[NX_n]} = K_2 \quad (2)$$

$$\frac{[M^{m+}][e^-]^m}{[Mem]} = K_3 \quad (3)$$

$$\frac{[N^{n+}][e^-]^n}{[Nen]} = K_4 \quad (4)$$

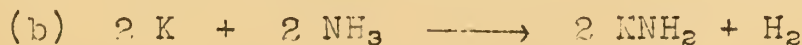
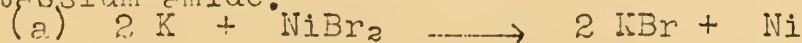
K_1 , K_2 , K_3 , and K_4 are the mass action functions for the above reactions. The nature of the reduction reactions will be affected by the respective mass action functions and by the solubility products of both the reactants and the products.

II. Early work in reduction of metals in liquid ammonia was done by Burgess and Rose (2). They found that sodium reacts with zinc (II) cyanide to precipitate the intermetallic compound $NaZn_4$.



When this compound reacts with oxygen sodium monoxide is formed rapidly after which zinc is oxidized slowly. The speed of reaction is increased in the presence of moisture or upon heating. $NaZn_4$ reacts with water to liberate 4.2 to 4.4 equivalents of hydrogen for each mole of $NaZn_4$; with HCl to liberate the theoretical 9 equivalents.

Burgess and Eastes (3) produced activated nickel by reduction of various nickel (II) salts. A competing reaction results in the formation of potassium amide.



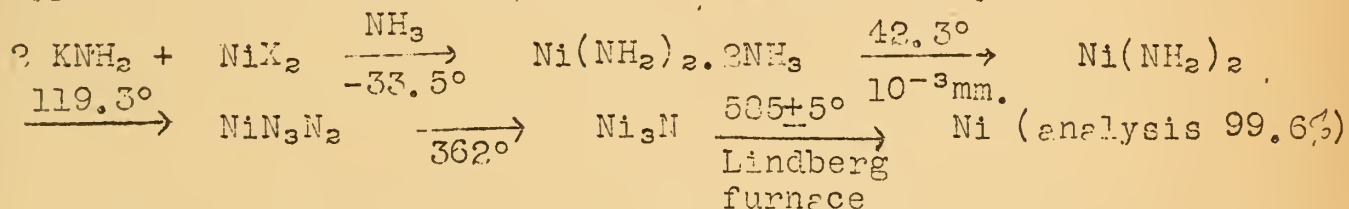
The extent to which the second reaction takes place can be calculated from the amount of hydrogen gas evolved. Nickel formed by calcium reduction was so effective as a catalyst for amide formation that most of the calcium was converted to calcium amide. Nickel produced by the action of sodium or potassium upon nickel thiocyanate was the most

finely divided and least efficient as a catalyst. The order of reactivity or catalytic effect for nickel produced from halides is given by the series: $\text{NiCl}_2 \ll \text{NiI}_2 < \text{NiBr}_2$.

III. Recent work: Watt and Moore (4) studied the reducing properties of Na_3Bi in liquid ammonia. It is used in the partial reduction of bismuth (III) oxide to bismuth, the complete reduction of ammonium ion to hydrogen, silver (I) iodide to silver, and bismuth (III) iodide to bismuth. It was found that 3.17 equivalents of sodium react with one equivalent of bismuth (III) iodide to give 96.2% bismuth (pyrophoric) and 3.1% sodium hydroxide. When the bismuth formed was treated in liquid ammonia with an excess of ammonium bromide to remove the sodium hydroxide, the final product contained 98.2% bismuth (non-pyrophoric) and 1.6% sodium hydroxide. This product gave X-ray diffraction pattern characteristic of bismuth.

Watt and Davies (5) identified the nature of by-products of the liquid ammonia reduction reaction of potassium with various nickel (II) salts. In the reduction of nickel (II) bromide and nickel (II) iodide with potassium in liquid ammonia large quantities of nickel (II) amide 2-ammoniate are formed if the potassium is added slowly in small pieces (Ni yield 55 to 83%). Nickel content increases and amide content decreases when potassium is added in large pieces as rapidly as possible. It was postulated for the first case that the concentration of potassium is great enough to form an appreciable amount of potassium amide which in turn reacts ionically with the nickel (II) ion to form nickel (II) amide 2-ammoniate. The purity of the nickel was found to decrease as the potassium to nickel (II) iodide ratio was increased. The nickel obtained from the reduction of nickel (II) iodide was non-pyrophoric. The rate of hydrogen adsorption for the forms of nickel decreased in the following order: Raney Ni > Ni from NiBr_2 (optimum conditions) > Ni from NiBr_2 (large scale run or heated to 130°) > Ni from $\text{NiBr}_2 + \text{KI}$ > Ni from NiBr_2 heated at 365°C .

Typical reactions are represented schematically as follows:



X-ray diffraction patterns of the final deammonation product showed exclusively the lines characteristic of face centered cubic nickel.

Bibliography

1. Kraus and Kurtz, J.A.C.S. 47, 43, (1925).
2. Burgess and Rose, Ibid. 51, 2127, (1929).
3. Burgess and Eastes, Ibid., 63, 2674, (1941).
4. Watt and Moore, Ibid., 70, 1197, (1948).
5. Watt and Davies, Ibid., 70, 3753, (1948).

FLUORIDES OF CARBON

Montfort A. Johnsen

April 18, 1950

A. INTRODUCTION

Although simple fluocarbons have been known since the work of Moissan, the highly specialized techniques necessary for their preparation, purification, and analysis have discouraged further investigations until recently. In 1941 it was realized that such compounds might prove useful as anti-foaming agents, nearly indestructible oils, greases, and plastics, and, most important, as improved carriers for UF_6 in gaseous diffusion processes. Government sponsored research programs were instigated to investigate these possibilities. Since then progress in fluocarbon chemistry has been very rapid.

B. NOMENCLATURE

A special method for naming fluocarbons and highly fluorinated substances has been proposed (1). The symbol " ϕ ", or phi, designates the prefix "perfluoro". Hence, perfluorohexane becomes ϕ hexane. Similarly, 1,1,1,2,3,3,4,4,5,5,6,6,7,7-tetradecafluoroheptane becomes 1,6-dihydro ϕ heptane, and ϕ succinic acid has the formula $(\phi \cdot CF_2 \cdot CO_2H)_2$.

C. PREPARATION OF FLUOCARBONS

Nearly all methods used to prepare fluocarbons involve elementary fluorine, either directly, or in the form of certain metallic fluorides which can be manufactured only by use of the gas (2). MnF_3 , CoF_3 , and BiF_3 are three of these fluorides. CoF_3 is most widely used.

I. Direct Fluorination Procedures:

The fluorination of graphite leads to the interstitial compound $(CF_n)_x$. This is a grey solid that explodes upon heating, giving simple fluocarbons and soot. The reaction is of no commercial importance.

From the reaction of lampblack with fluorine, fluocarbons from ϕ methane to ϕ heptane have been isolated. At room temperature about 35% of the product is gaseous.

Direct gas phase fluorination of hydrocarbons has been considered. At high temperatures combustion occurs, the main products being HF and CF_4 . At low temperatures HF and a resinous, highly fluorinated polymer result.

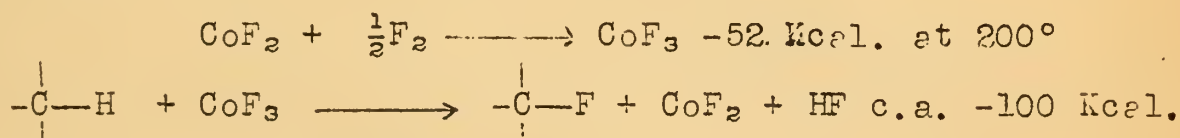
Fukahara and Bigelow (3) were able to control this process using a low temperature catalytic reaction. In the present method, developed by Cady, et.al. (4), vaporized hydrocarbon and fluorine, both diluted with nitrogen, are led through pipes three inches apart into a reaction tube and allowed to percolate through several feet of silver coated copper chips. The reactor is maintained at 150° to 200°, and a slight excess of fluorine is used to insure complete fluorination. Statistics for representative runs are given:

| Material Fluorinated | Temperature | Product | Yield |
|--|-------------|---------------------------------|-------|
| C ₆ H ₆ | 265 | C ₆ F ₁₂ | 58% |
| n. Heptane | 135 | C ₇ F ₁₆ | 62% |
| C ₆ H ₅ ·CF ₃ | 200 | C ₇ F ₁₄ | 85% |
| C ₆ H ₅ ·(CF ₃) ₂ | 200 | C ₈ F ₁₆ | 87% |
| Anthracene | 300 | C ₁₄ F ₂₄ | 43% |

The crude product is collected at -78°. Fluocarbons are immiscible with HF and are withdrawn at the bottom of the trap, washed with alkali, dried with Na₂SO₄, and carefully distilled.

II. Indirect Fluorination Procedures:

The replacement of a hydrocarbon hydrogen by fluorine produces about 150 Kcal. This is sufficient to cause cracking. Thus it is often advantageous to conduct fluorinations in two steps. These reactions are given for cobalt fluorides:



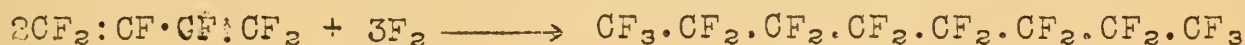
In a typical process (5) a four inch revolving reactor tube about eight feet long is half-filled with CoCl₂. The cobalt (II) compound is converted to CoF₂ at 450° by HF and further oxidized to CoF₃, using fluorine. The hydrocarbon, diluted with HF or nitrogen, is passed through the tube at 250°, and the products collected and processed as before. n. Heptane gives φ n.heptane in 87% yield.

Since fluorine is costly, hydrocarbons are often partially fluorinated with SbF₃Cl₂, BrF₃(6), PbF₄(7), and similar agents before treatment with CoF₃.

III. Special Techniques:

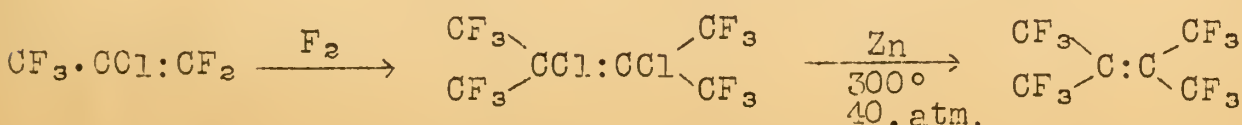
Olefinic fluocarbons are readily produced by dehydrohalogenation and related reactions. Such compounds, surprisingly, are quite active. Ethylene, for example, upon heating to 200° under special conditions, gives Teflon. Heating to 700° gives a number of products. These pyrolysates are usually cyclic structures which may or may not have side-chains, (8). It has recently been shown that no φ cyclopropene is obtained (9).

φ Butadiene, like its hydrogen analog, can be polymerized (10), but to a lesser extent. If fluorine is used as the condensing agent, either fluorine or a perfluorinated radical can be added as double bonds are opened. For example:



The compounds C₈F₁₈, C₁₂F₂₆, C₁₆F₃₄, and C₂₀F₄₂ have been prepared in this manner.

Fluorine may be used to condense other olefinic compounds:



If desired, the product, φ 2,3-dimethyl-butene-2, can be fluorinated to give φ 2,3-dimethylbutane, (10).

D. PROPERTIES OF FLUOCARBONS

Complete substitution of hydrogens in hydrocarbons by atoms of fluorine causes a relatively small change in the boiling point and melting point. The boiling points of ϕ alkanes having more than five carbons are actually lower than those of the hydrocarbons. Densities are normal and lie between 1.5 and 2.0 gm./cc. Up to C_6 the fluocarbons are gases at room temperature, from C_7 to C_{12} they are colorless liquids, and above C_{12} they are white, waxy solids. Cyclic compounds above C_6 , however, are solid.

The fluocarbons decompose at red heat to give CF_4 and carbon. They react with sodium and Mischmetall only above 350° unless unsaturated. Other reagents are without effect. They are soluble in only a few solvents, such as CCl_4 , and $CCl_3 \cdot CClF_2$.

Polymerization can be controlled to give the equivalent of any hydrocarbon product; i.e. motor oils, greases, etc. Such substances have now been prepared in ton lots using techniques described above. Because of these and many other interesting and useful properties of fluorine containing organic compounds it is predicted that there will continue to be an increasing academic and industrial interest in fluorine chemistry.

BIBLIOGRAPHY

1. J. H. Simons; Ind. and Eng. Chem. 39, 240, (1947).
2. "Die Chemie des Fluors", Ruff, page 50, Julius Springer, Berlin, 1920.
3. Fukahara and Bigelow; J. Am. Chem. Soc. 63, 2792, (1941).
4. Cady, et.al.; Ind. and Eng. Chem. 39, 290 (1947).
5. Grosse, et.al.; Ind. and Eng. Chem. 39, 314 (1947).
6. Ligett, et.al.; U.S. 2,487,820; Nov. 15th, 1949.
7. Smith and Hines; U.S. 2,480,080; Aug. 23, 1949.
8. Park, Benning, et.al.; Ind. and Eng. Chem. 39, 354, (1947).
9. Young and Murray; J. Am. Chem. Soc. 70, 2814, (1948).
10. Booze and Ruff; Z. allgem. anorg. Chem. 217, 1, (1937).

FORMATION AND STABILITY OF BINARY INORGANIC COMPOUNDS

William W. West

April 25, 1950

Introduction. Pauling (1) has shown how to calculate the heat of formation of the simplest covalent compounds; for partially ionic compounds a correction for the ionic part of the bond must be made. The heat of formation ΔH_e of ionic compounds AX_n can be found by the use of the Born-Haber cycle

$$\Delta H_e = -S -I -D +E +U$$

provided that certain quantities are known, namely sublimation energy S and ionization energy I of element A and electron affinity E and dissociation energy D of element X --- U , the crystal energy being calculated. Van Arkel (2,3) has pointed out that these heats of formation can be calculated fairly accurately with less complicated compounds, and he has also pointed out the way in which the heat of formation varies with radius, charge and electronic configuration of the ions. In some respects, the heat of formation is a measure of the stability of a compound.

Normal Ionic Compounds. Normal ionic compounds are defined by van Arkel as compounds in which the valency of the positive ion is equal to the number of valency electrons, i.e. ions having two, eight or eighteen electrons, s^2 , s^2p^6 , $s^2p^6d^{10}$ in the outermost electron shell. The first two types are "rare gas ions" and the last are called "eighteen electron ions". The term "normal ionic compounds" does not refer to a bond type which is necessarily purely ionic, but is used in contradistinction to normal covalent compounds, where a formula can be found in which both atoms have an octet structure.

Generalizations. The heat of formation per gram equivalent for binary compounds containing a positive ion with a rare gas configuration obeys the following general rules

(1) it increases with increasing radius of the positive ion, with the exception of the hydrides, fluorides, oxides and nitrides of the alkali metals and the largest alkaline earth metals, in which the radius of the negative ion is not large compared with the positive ion

(2) it decreases with increasing radius of the positive ion, in one period of the system, except that in fluorides, oxides and nitrides there is a maximum in the second or third group, when the positive ion is large

(3) substitution of an ion of rare gas configuration by one with eighteen electron configuration always decreases the heat of formation

The following rule applies to negative ions

(4) the heat of formation decreases (a) if the radius of the negative ion increases and (b) if the charge of the negative ion increases

Dependence of ΔH_e on the radius of the positive ion. The increase of the heat of formation with increasing radius of the positive ion (see (1) above) is due primarily to the lowering of the ionization energy I , which is however counteracted by the decrease in crystal energy U . The influence of the crystal energy is less when the positive ion is small, so that when the valency is high the heat of formation always increases

when a positive ion with rare gas structure is replaced by a larger one. The effect of crystal energy predominates only when a large positive ion is combined with a small negative one.

The decrease of the heat of formation with increasing charge of the positive ion (see (2) above) is caused mainly by the rapid increase of the ionization energy counterbalanced by the increase in crystal energy. The maximum mentioned in (2) appears when the increase of crystal energy is very rapid (e.g. in oxides and nitrides). The increase is due both to an increasing charge and to an increasing Madelung constant A , a constant depending on charge and on the geometry of the crystal. When the crystal energy is smaller, due to the greater radius of the negative ion, the increase in the heat of formation (as in the sulfides, e.g. Cs_2S to La_2S_3) is much smaller and no maximum is observed. For the halides the Madelung constant decreases in the sequence AX , AX_2 and AX_3 . In this group maxima are observed only for the fluorides, where the crystal energy is high because of the small radius of the F^- ion.

Dependence of ΔH_f on electron configuration. In the last seven groups of the periodic system the heats of formation are very complex functions of radius, charge and configuration of the ions. In the elements following copper, silver and gold in the fourth, fifth and sixth periods the ionization energy is not a continuous function of the radius of the positive ion as in the first groups. Ions with an eighteen electron configuration have a greater ionization energy than ions with a rare gas configuration of equal size ($I_{\text{Ag}} > I_{\text{Na}}$), an effect which is due to imperfect screening of the charge by the eighteen electron shell. This increased ionization energy of the eighteen electron ion is accompanied by an increase of crystal energy in its compounds. The latter effect will always be the smaller, however, and the compounds containing eighteen electron groups will have lower values of ΔH_f . With very high ionization energies (e.g. Au), a very sharp decrease in the heat of formation is observed, sometimes leading to instability of the compound (AuCl). A similar effect is encountered with the thirty-two electron shell. The heat of formation increases in passing from an element of the second period to the third, due to increased radius of the positive ion (still a rare gas structure). There is a decrease from the third to the fourth because of the transition from an eight electron shell to one with eighteen electrons, followed by an increase from the fourth to the fifth (increasing radius of the positive ion). From the fifth to the sixth period (antimony to bismuth) there is once more a decrease in heat of formation, caused by the imperfect screening of the complete N shell with thirty-two electrons.

BIBLIOGRAPHY

- (1) Pauling, L., Nature of the Chemical Bond, Cornell University Press, 2nd ed., New York (1948)
- (2) Van Arkel, A. E., Molecules and Crystals, Interscience Publishers Inc., New York (1949)
- (3) Van Arkel, A. E., Research 2, 307-13 (1949)

CUPROUS CHLORIDE COMPLEXES OF MALEIC AND FUMARIC ACIDS

David Carley

April 25, 1950

Recently a great many studies have been made to determine the relative tendencies of different olefins to form cuprous chloride complexes. Particular attention has been paid to the influence which the substituents at the double bond exert on the complex. Investigators at the University of California (1) have compared the degree to which cis-trans isomers, such as maleic and fumaric acids form such complexes.

The procedure for determining the formation of the complexes is similar to that carried out by Kepner and Andrews (2) in determining the solubility of cuprous chloride in allyl alcohol. In these experiments it was shown that 1-1 complex ($\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}\cdot\text{CuCl}$) was formed. By shaking solid cuprous chloride with partially neutralized F. (fumaric acid) and H_2M (maleic acid) in various hydrogen-ion concentrations, a yellow crystalline solid formed in each case. When dissolved in HCl , and titrated for cuprous ion content (3) it was found that in the case of H_2M , cuprous acid maleate dihydrate was the yellow solid. And the solid itself gave negative tests for sodium and chloride ions. In the case of H_2F , the yellow solid was never isolated free from cuprous chloride. Because of the complications arising from this cuprous salt formation, no solubility studies were made on partially neutralized acids.

Experiments were carried out to establish that the reaction conditions of the solubility determinations were not conducive to cis-trans isomerism--i.e., that H_2M had not changed over to H_2F due to acid catalysis by the CuCl .

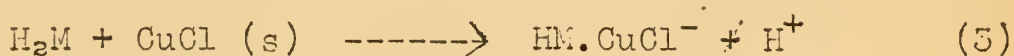
In the case of H_2F , it was found that as the hydrogen-ion concentration, $[\text{H}_2\text{SO}_4]$, decreased, K_1 for the reaction remained almost constant.



Two series of solubility measurements were made using H_2M solutions. One involved various H_2SO_4 concentrations--the other, various HClO_4 concentrations. In this case, as the hydrogen-ion concentrations decreased, the values of K_1 increased markedly. This was explained on the basis of the following equilibria.



$$K_2 = \frac{a_{\text{H}_2\text{M}\cdot\text{CuCl}}}{a_{\text{H}_2\text{M}}}$$



Here, a value for K_3 was obtained. K_4 represented the reaction



and was taken from previous data. Its value was 0.014.

Through various other equations, involving the concentrations of the complex, maleic and fumaric acids, an equation was derived which involved all the K values and activity coefficients.

$$K_1 \left[1 + \frac{K_4 \gamma_{H_2M}}{\gamma_H \gamma_{HM} [H^+]} \right] = \frac{K_2 \gamma_{H_2M}}{\gamma_{H_2M} \cdot CuCl} + \frac{K_3 \gamma_{H_2M}}{\gamma_H \gamma_{HM} \cdot CuCl^- [H^+]} \quad (5)$$

In all computations it was assumed that γ of uncharged molecules was unity. The left hand side of the equation was plotted versus $1/\gamma_H \gamma_{HM} \cdot CuCl^- [H^+]$ and a straight line resulted. The intercept of the line was $K_2(0.083)$ and the slope equal to $K_3(0.0043)$. $HClO_4$ and H_2SO_4 gave similar results, indicating merely that the source of the hydrogen-ion concentration was not critical.

K_2 for H_2M (0.083) was found to be less than K_1 for H_2F (0.31), and it therefore complexes cuprous chloride to a lesser extent than H_2F . For $HM \cdot CuCl^-$, K_3 was found by subtracting equation (4) from equation (3). Its value was 0.31. Therefore HM^- complexes $CuCl$ more than H_2M does.



The Absorption Spectra

Evidence for the conclusions as to the structure of the complexes, based on the solubility experiments, was supported by measuring the absorption spectra of the yellow complex solutions.

By showing that solutions of cuprous chloride and sulfuric acid or H_2X had little or no absorption in the range 320-400 mμ, it was established that the absorption would be due to the complex itself.

Within limits of experimental error, spectra of the solutions obtained by shaking cuprous chloride with solutions of fixed H_2F concentrations were identical although the H_2SO_4 concentrations were varied. At very low sulfuric acid concentration the position of the absorption maximum shifted toward the ultra-violet and the maximum optical density was somewhat less. This was presumably due to the formation of some $HF \cdot CuCl^-$.

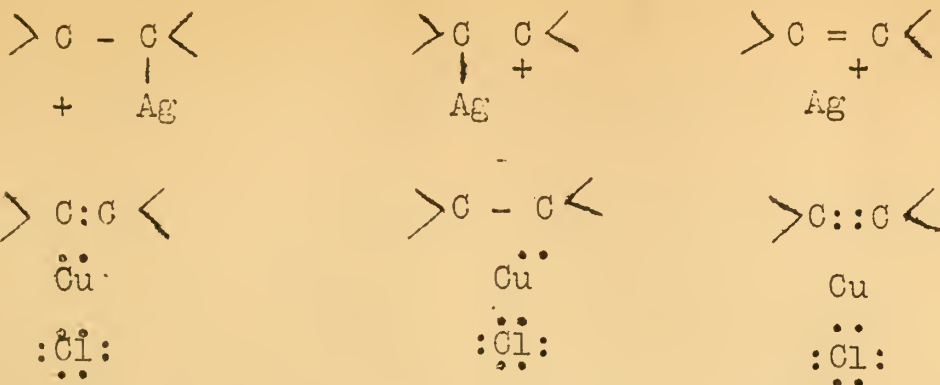
Using H_2M solutions of the same concentration, the optical densities increased even with a small decrease in sulfuric acid concentration. When the sulfuric acid concentration was further decreased, the position of the absorption maximum shifted toward the visible, and the optical densities increased greatly. This showed that considerable amounts of $HM \cdot CuCl^-$ were formed even in reasonably high hydrogen-ion concentration, and it appeared that the extinction coefficient for $HM \cdot CuCl^-$ was considerably larger than for $H_2M \cdot CuCl$.

These measurements corroborated the solubility experiments which showed that considerable amounts of $HM \cdot CuCl^-$ were formed.

For solutions of $H_2F \cdot CuCl$, the optical density was directly proportional to the original H_2F concentration -- i.e., conformed to Beer's law. This was possibly further evidence of a 1-1 complex.

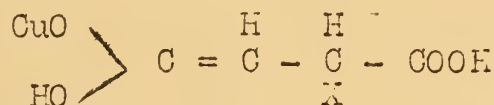
The extinction coefficients were computed and found to be 1900 for $H_2F \cdot CuCl$, 2000 for $H_2M \cdot CuCl$, and 3800 for $HM \cdot CuCl^-$.

From all the experimental results it seemed reasonable to classify the complexes as the metal-olefin type (4). To base this type of bond on the theory of electron pair bonds, a satisfactory structure is obtained by considering a resonance among three forms.



Since both H_2F and H_2M readily form cuprous chloride complexes, it is unlikely that the structure of the maleic acid complex is of the chelate type, in which both carbonyl groups are concerned.

Since there is no isomerization of H_2M to H_2F , it is unlikely that an intermediate structure due to acid catalysis by the cuprous chloride exists. (5)



Summary

Solubility measurements of cuprous chloride in fumaric acids indicate the formation of 1-1 complexes. With H_2F , the complex is of the type $H_2F.CuCl$. With H_2M , evidence was found for the formation not only of $H_2M.CuCl$ but also $HM.CuCl^-$ ----- even in solutions of reasonably high hydrogen-ion concentration. Supporting evidence was obtained through absorption studies.

REFERENCES

- (1) Andrews, L. J. and Kiefer, R. H., J. Am. Chem. Soc., 70, 3361 (1948)
- (2) Andrews and Kepner, J. Org. Chem., 13, 208 (1948)
- (3) Hatch and Estes, J. Am. Chem. Soc., 67, 1730 (1945)
- (4) Winstein and Lucas, J. Am. Chem. Soc. 60, 836 (1939)
- (5) Nozaki and Ogg, J. Am. Chem. Soc. 63, 2583 (1941)

Complexes between Metal Salts and Long-chain Aliphatic Amines

Sheldon S. Simon

May 2, 1950

The relative stabilities, properties, and reactions of complexes of uni- and bi-valent copper salts with long chain primary aliphatic amines have been studied recently by Burkin and coworkers (1). Particular attention was paid to the effects of (a) the anion used, (b) the basicity of the amine, and (c) the nature of the solvent.

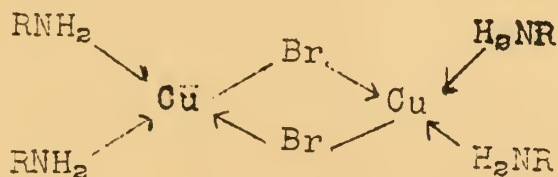
Results show that copper salts on refluxing with an aliphatic primary amine in an organic solvent form complexes in which the acid radicals are covalently bound to the copper atom and that the coordination number of four is maintained for copper. This behavior is not observed for the copper complexes with lower amines, such as ethylamine and ammonia. It is believed to be due to solvents used and not to a fundamental change in the nature of the copper-acid radical links caused by increasing the molecular weight of the amine.

Cupric salts give complexes represented by the formula $\text{CuAn}_2(\text{RNH}_2)_2$, where R = a long chain amine and $\text{An} = \text{Cl}^-$, Br^- , CH_3COO^- , $(-\text{CH}_2\text{COO})_2^-$, $[-(\text{CH}_2)_2\text{COO}]^-$, and SO_4^- .

Burkin and Wilkins (2) have been able to prepare coordination complexes of cuprous salts with the higher primary aliphatic amines. Cuprous chloride and iodide form only monamine complexes possessing the empirical formulae $(\text{CuCl} \cdot \text{RNH}_2)$ and $(\text{CuI} \cdot \text{RNH}_2)$ even though almost two moles of amine per mole of Cu(I) compound were required to effect their preparation. Cuprous bromide forms a monamine complex, $(\text{CuBr} \cdot \text{RNH}_2)$, if only one mole of amine was allowed to react per mole of cuprous bromide. In the presence of two mole of amine a bisamine complex, $(\text{CuBr} \cdot 2\text{RNH}_2)$ was formed.

The empirical formula of the cuprous halide complexes would lead to the conclusion that the coordination numbers for copper(I) may be two or three; however, polymerization occurred in all cases demonstrating that the usual stable coordination number four had been attained in these compounds. The monamine complexes were shown to have a tetrameric structure. The polymeric structures are believed to be due to the fact that halogen atoms act as bridging groups between the metallic atoms (3).

The bisamine complexes of cuprous bromide were shown to have a dimeric, presumably bridged structure at low temperatures.



$\text{R} = \text{C}_{12}\text{H}_{25} \text{ and } \text{C}_8\text{H}_{17}$

At higher temperatures dissociation occurs into the monamine complex and free amine. The solid bisamine complex reforms and separates on cooling.

Air oxidation occurred (4) when tetrakis - cuprous chloride (or bromide) monamine,, dissolved in a non-aqueous solvent such as benzene or chloroform is refluxed with the corresponding amine hydrochloride (or hydrobromide). A cupric chloride (or bromide) amine complex is formed ($\text{R} = \text{C}_8\text{H}_{17}$, $\text{C}_{12}\text{H}_{25}$; $\text{X} = \text{Cl}$ or Br):

EX-100

[Faint, illegible markings]

[illegible]

PHASE EQUILIBRIUM OF THE SYSTEM SULFUR TRIOXIDE AND WATER

L. F. Audrieth

May 2, 1950

An equilibrium solubility method, involving determination of the composition of a liquid phase in equilibrium with a known solid phase was used in conjunction with the method of thermal analysis to redetermine values for freezing points in the system $\text{SO}_3\text{-H}_2\text{O}$ from 0 to 93.7% SO_3 . Congruent melting points are given for the following compounds in this system: $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$, -28.36° ; $\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$, -39.51° ; $\text{H}_2\text{SO}_4\cdot \text{H}_2\text{O}$, 8.56° ; H_2SO_4 , 10.37° ; $\text{H}_2\text{S}_2\text{O}_7$, 35.15° . The hydrates $\text{H}_2\text{SO}_4\cdot 6\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4\cdot 3\text{H}_2\text{O}$ undergo transitions to the tetrahydrate at -53.73° and -36.56° , respectively. Complete diagrams are given in reference (1).

The system $\text{SO}_3\text{-H}_2\text{O}$ is complete except for the range between 95-100% SO_3 . This portion of the system must be exceedingly complex as pure SO_3 by itself exists in no less than three different modifications. The beta and gamma forms are metastable with respect to the highly polymerized alpha form as indicated by data for heats of fusion and of sublimation, and the vapor pressures of each. Distillation of small amounts of SO_3 from the high polymer leaves residues whose initial melting points gradually increase from 62.3°C . upward. The high polymer melts to a liquid which is identical with that of the gamma form. Melting of the alpha form must be carried out with care since explosive vaporization may occur.

Polymerization of the gamma form is induced by the catalytic action of water. The process involves initiation, propagation and termination of the polymerization reaction. "Chain breakers" include substances such as S, Te, CCl_4 and POCl_3 which inhibit polymerizations. Stabilized forms of sulfur trioxide are now marketed under the trade names Sulfan A, B, and C corresponding roughly to the beta, gamma and alpha modifications.(2).

References:

- 1) Gable, Betz and Maron, J. Am. Chem. Soc. 72, 1445 (1950).
- 2) "Sulfan," descriptive folder issued by the General Chemical Company.

ELECTROCHEMICAL STUDIES OF SOME COORDINATION COMPOUNDS OF IRON

Ward B. Schaap

Thesis Report

May 9, 1950

Studies have been carried out dealing with the complexes of ferric and ferrous ions with a number of dicarboxylic acids - oxalic, malonic, succinic, glutaric and β -substituted glutaric acids. The bivalent anions of these acids form a series of complexing agents of gradually increasing size, making it possible to evaluate the effect of the size of the complexing groups on the composition and stability of the resulting complexes.

Electrochemical data were obtained by means of the polarograph. The location of the waves (i.e. the half-wave potentials) are related to the formulas and stabilities of the complexes when the reductions proceed reversibly (1).

In the case of iron and oxalate ion, one ferric and two ferrous complexes were found to exist. This result confirms the work of Lingane (1) rather than that of Stackelberg and Freyhold (2), whose data indicate only one complex in each valence state. Since the polarographic data, in this case, yield only the ratio of the dissociation constants of the complexes in the oxidized (FeIII) and reduced (FeII) states and indicate only the difference in the number of complexing groups attached to each, an independent method is needed to fix the formula and dissociation constant of any one of the complexes before the values for the others can be obtained. To obtain the dissociation constant for the ferric complex, which is known to be the trioxalato ferrate (III) ion, base was added to solutions containing ferric iron and known concentrations of oxalate ion until a precipitate of ferric hydroxide was present. The dissociation constant was calculated by means of the equation

$$K_d = \frac{(K_{sp}) [\text{Ox}^{--}]^3}{[\text{Fe}(\text{Ox})_3^{--3}] [\text{OH}^-]^3}$$

where the K_{sp} of ferric hydroxide and the oxalate concentration are known; the hydroxide ion concentration measured and the concentration of soluble complex obtained from the polarographic diffusion current. The following complexes and dissociation constants were found:

| | | |
|---|-------------------------|---------------------------|
| $\frac{[\text{Fe}(\text{OX})_3^{--3}]}{[\text{Fe}(\text{OX})_3^{--4}]}$ | $K = 4 \times 10^{-18}$ | |
| $\frac{[\text{Fe}(\text{OX})_3^{--4}]}{[\text{Fe}(\text{OX})_2^{--2}]}$ | 2×10^{-5} | $(>0.2M \text{ OX}^{--})$ |
| | 1×10^{-4} | $(<0.2M \text{ OX}^{--})$ |

The complexes of iron with malonate ion were studied similarly. The independent method used to establish the formula and stability of the ferric complex was similar to that used in the oxalate study, except that the formulas were generalized to take into consideration the possible formation of a basic complex or precipitate.

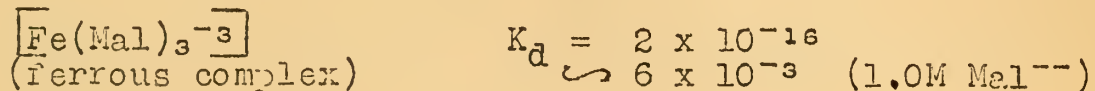
Precipitate: $\text{Fe}(\text{Mal})_a(\text{OH})_b$ $K_{sp} = [\text{Fe}^{+3}] [\text{Mal}^{--}]^a [\text{OH}^-]^b$

Complex: $[\text{Fe}(\text{Mal})_c(\text{OH})_d]$ $K_d = \frac{[\text{Fe}^{+3}] [\text{Mal}^{--}]^c [\text{OH}^-]^d}{[\text{complex}]}$

Hence $K_d = \frac{(K_{sp}) [\text{Mal}^{--}]^n}{[\text{complex}] [\text{OH}^-]^m}$

and $\log \frac{K_d}{K_{sp}} = n \log [\text{Mal}^{--}] - m \log [\text{OH}^-] - \log [\text{complex}]$

Graphical plots of the data, where one of the variables was held constant, indicate that $m = 3$ and $m/n = 1$. It was concluded that (if the precipitate and complex were not polynuclear) the precipitate is ferric hydroxide and the complex is the tris (malonato) ferrate (III) ion. Assuming this formula for the ferric complex, the experimental data, taken at face value, yield the result that the ferrous-malonate complex in dilute malonate solutions (0.02 to 0.3M) has a ratio of 1 1/2 malonate groups to each ferrous ion. Either a binuclear complex is indicated, or else the weakness of the ferrous complex ($K_d = 10^{-2}$ to 10^{-3}) causes the value obtained to be an average of the complex and free ferrous ions. This is being investigated further. Results for the iron malonate system are:



It was observed that the polarographic diffusion currents decreased markedly with increased potassium malonate concentration, the value in 3M solutions being somewhat over half of the value in dilute solutions (0.1M). Thus, either the diffusing ion is changing in composition, or some property of the solution is changing and affecting the diffusion of that ion. The following relation between the diffusion current constant (d_{cc}) and the viscosity coefficient of the solution relative to water (η) was derived and found to fit the experimental data reasonably well.

$$d_{cc} \cdot \eta^{\frac{1}{2}} = \text{constant}$$

Incomplete investigation of the iron-succinate system shows that the iron succinate complexes are considerably weaker than the oxalate and malonate. In solutions of similar concentration and pH to those used above, no soluble ferric complexes were found in solution, all the iron present being precipitated. Upon addition of excess acid a colorless solution can be obtained which shows a reduction wave around zero applied potential (vs.S.C.E.), presumably due to reduction of the tris (succinato) ferrate (III) complex. At the higher pH values, addition of more succinate produced yellow or tan solutions giving one or two reduction waves at more negative potentials. These waves appear to be pH dependent and probably result from reductions of basic complexes, the large size of the succinate ion causing the tris(succinato) ferrate (III) complex to be unstable to the substitution of small hydroxide ions for succinate ions under these conditions.

The contemplated study of glutarate and β -substituted glutarate complexes purposes to determine the effect that substitution on the chain has on the stability of the complexes, since such substitutions do affect the acid ionization constants and, presumably, the inter-carboxyl distance (3).

- (1) Kolthoff and Lingane, Polarography, Interscience (1941)
- (2) Stachelberg and Freyhold, Z. Electrochem., 46, 120 (1940)
- (3) MacInnes, Principles of Electrochemistry, Reinhold (1939)

AUTOKIDATION OF HYDRAZINE

Paul H. Mohr

Thesis Report

May 9, 1950

Dilute aqueous solutions of hydrazine have been found to undergo deterioration in the presence of atmospheric oxygen (1,2) and in contact with various metallic surfaces (3). The autoxidation reaction has been subjected to a more extended study a) to determine the influence of such factors as concentration of hydrazine, pH, and presence of metallic ions on the rate of oxidation and b) to develop inhibitors to stabilize hydrazine.

Hydrazine is a weak base, a polar compound, a powerful reducing agent, and a good coordinating agent. Hydrazine is also the parent substance of a system of compounds. Reactions involving hydrazine will change as the nature of the medium is varied from dilute aqueous solutions to the highly concentrated base. Hydrazine is a hydronitrogen and is being considered as a speciality fuel. It is the nitrogen analog of ethane. It is significant that hydrocarbon fuels are subject to autoxidation and that this reaction with atmospheric oxygen, leading to development of acidity and sludge formation, is catalyzed by trace quantities of various dissolved metals.

EXPERIMENTAL

A. Autoxidation of Dilute Aqueous Hydrazine

The oxidation of dilute aqueous hydrazine solutions by molecular oxygen was first studied by Gilbert (1) who demonstrated that the process is heterogeneous in nature and that the overall reaction may be represented by the equation:



Traces of hydrogen peroxide are formed as an intermediate product. Brown (2) subsequently found that small amounts of copper accelerate markedly the autoxidation reaction.

The author has found that copper is unique in its catalytic action. Such metals as chromium, cobalt, nickel, manganese, and iron in the dissolved state exert little or no influence on the extent of autoxidation. The rate of the reaction appears to be some function of the dissolved copper concentration, since the percentage of hydrazine oxidized increases as the amount of added copper (as CuCl_2) is increased up to 10^{-4} M (for a 0.5 M hydrazine solution). Above this limiting concentration visible reaction results in the formation of a red precipitate of metallic copper and some cuprous oxide, presumably from disproportionation of the cuprous ion.

Both Brown (2) and Gilbert (1) had found that the autoxidation rate of dilute aqueous hydrazine solutions varies with pH and passes through a maximum at a pH equivalent to 0.01 M to 0.03 M sodium hydroxide. The author was only able to duplicate this observation when traces of copper were present.

In order to reduce the catalytic influence of copper on the autoxidation of hydrazine, the following classes of substances were evaluated:

1. Precipitating agents which form very insoluble cuprous or cupric compounds.

2. Complexing agents which coordinate strongly with the cuprous or cupric ion.
3. Adsorbents which are effective in destroying the catalytic influence of copper in other systems.

These materials were evaluated by subjecting 0.5 M hydrazine solutions containing 10^{-4} M dissolved copper and 10^{-2} M inhibitor to the action of oxygen. Typical results for the percentage of hydrazine oxidized in 24 hours under the given experimental conditions are presented in Table 1. Potassium ethylxanthate, thiourea, sodium cyanide, sodium sulfide, and sodium thiocyanate are outstanding inhibitors (copper deactivators).

Table 1

THE COMPARATIVE EFFECTIVENESS OF VARIOUS COPPER
DEACTIVATORS ON THE AUTOXIDATION OF DILUTE HYDRAZINE SOLUTIONS

(Original N_2H_4 concentration: 0.500 M; deactivator concentration: 1×10^{-2} M; Cu concentration: 1×10^{-4} M; time: 24 hr.)

| Copper Deactivator | Per Cent N_2H_4 Oxidized |
|---------------------------|---|
| Potassium ethylxanthate | 4.0 |
| Sodium stearate | 8.1 |
| Thiourea | 11.2 |
| Sodium cyanide | 12.8 |
| Sodium sulfide | 13.8 |
| Sodium thiocyanate | 14.0 |
| Ethylenediamine | 20.2 |
| Gelatin | 29.6 |
| O-Phenanthroline | 31.2 |
| Glycine | 48.2 |
| Stannic chloride | 80.2 |
| Sodium pyrophosphate | 86.8 |
| Ammonium aluminum sulfate | 96.0 |
| Mannitol | 96.0 |
| Blank | 97.9 |

B. Autoxidation of Concentrated Hydrazine

Whereas a static procedure was employed in studying the autoxidation of dilute hydrazine solutions, a dynamic method was used throughout the investigation of the essentially anhydrous base. The observations made in the more concentrated hydrazine were found to be comparable to those obtained in the earlier investigation.

Copper was again found to be unique in its catalytic action. Such dissolved metals as chromium, vanadium, cobalt, nickel, and iron exerted no catalytic action whatsoever. It was observed that a larger quantity of copper was capable of dissolving in the more concentrated hydrazine. Concentrations as high as 10^{-3} M cupric chloride were completely soluble in 30 M hydrazine and no visible signs of reaction were noted until autoxidation had reduced the hydrazine concentration to approximately 7 M.

Reduction in concentration of the catalytically active copper species by the use of precipitating or complexing agents served to inhibit the autoxidation of concentrated hydrazine. The choice of inhibitor in concentrated hydrazine was, however, much more critical than in the dilute aqueous solutions. Competitive complexing action of

hydrazine for the copper ion and solvolytic effects have to be taken into consideration. Copper deactivators which are particularly effective in concentrated hydrazine include sulfur, sodium sulfide, thiourea, sequestrane, sodium thiocyanate, and potassium ethylxanthate.

THE NATURE OF THE REACTION

The reaction between hydrazine and molecular oxygen is a typical autoxidation process. Hydrogen peroxide is formed as an intermediate product; the reaction is markedly catalyzed by dissolved copper, and the catalytic action can be overcome by the use of inhibitors (metal deactivators).

Several observations show evidence for the type of mechanisms involved. That the oxidation process is stepwise is indicated by the formation of trace amounts of hydrogen peroxide in the dilute aqueous solutions of hydrazine. This intermediate may be stabilized by adding small amounts of "chain breakers" (8-hydroxyquinoline and para tertiary butylcatechol). All of the dissolved copper in hydrazine solutions is present in the univalent state; in the essentially anhydrous medium the metal ion must exist primarily as the hydrazine complex. It can be postulated that the autoxidation involves a mechanism in which the copper (I) hydrazine complex participates as the catalytically active species. It is conceivable that a copper (I)-copper (II) redox mechanism can be set up in which the copper (I) complex is oxidized to the copper (II) state and the latter is in turn promptly reduced by hydrazine to the univalent form.

BIBLIOGRAPHY

1. Gilbert, J. Am. Chem. Soc., 51, 2744 (1929)
2. Brown, Thesis, University of Illinois, 1946.
3. Jolly, Thesis, University of Illinois, 1949.

8-Quinolinol and Substituted 8-Quinolinol Chelates of Certain Rare Earth Elements

Dale E. Jackson

May 16, 1950

I. Introduction

The preparation of chelates of the rare earth elements with 8-quinolinol (henceforth referred to as oxine) has been reported by several investigators (2,7,8,9,10). Attempts to repeat these experiments in this laboratory have met with only nominal success (3). The oxinates have been suggested for use in the gravimetric and volumetric determination of the rare earths; they represent one of the few examples of inner complexes of these elements; therefore further investigation was warranted.

Among a representative group of the rare earths a very slight chloroform solubility has been demonstrated only for ytterbium oxinate (3); however, the compounds formed with 5,7-dichloro-8-quinolinol (dichloroxine) exhibit much greater solubility. An investigation was therefore undertaken designed to coordinate observations on the absorption spectra of aqueous solutions of rare earth salts, and of solutions of the chelates. Similar observations on non-aqueous solutions of the 2,4-pentanedione complexes of neodymium and samarium have been recorded (12).

II. Studies on the Solid Compounds

A. Preparation and Properties of Oxine Chelates

Oximates are precipitated when a mixture of oxine and the cation in question is either formed at, or brought up to a pH at which precipitation of the hydroxide takes place. Since the heat-accelerated decomposition of urea in water solution causes a gradual rise of the pH numerous mixtures of rare earths and oxine were precipitated by boiling in the presence of urea. Analysis of the dried, yellow powders by quantitative bromination (6) and ignition of aliquots showed them to have an insufficient oxine content for the expected formula, $RE(C_9H_6ON)_3$. Other approaches were used, but with negative results until a slightly acidic mixture of oxine and $SmCl_3$ was treated with dilute NH_4OH without external heating. The precipitates were greenish-yellow and flocculent in appearance but turned dark green when dried at $130^\circ C$. Ignition analysis proved the samarium content to be within one per cent of theoretical.

No accurate melting or decomposition points for these substances have yet been obtained. Qualitative tests have shown only a partial solubility for the dried materials in chloroform and other organic liquids.

B. Preparation and Properties of Dichloroxine Chelates.

The urea method also failed in this case as did all other procedures which involved the use of excessive heating during the formation of the precipitates. Preparation of these substances at room temperature, on the other hand, by addition of NH_4OH or KOH to the unbuffered mixtures of rare earth and oxine led to successful isolation of the desired compounds. The resulting oximates are dark green when no excess dichloroxine is present. They may be dried at

much higher temperatures than the oxinates; however, 130°C. is adequate.

Although final data are still unavailable, the anhydrous dichloroxine chelates do not appear to be completely soluble in chloroform.

III. Studies on Chloroform Solutions of Oxine and Dichloroxine Chelates

A. Methods of Preparation

The original experiment involved extraction of NdCl_3 solution, buffered with $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ at a pH above that for precipitation of the hydroxide, with a chloroform solution of dichloroxine. Later preparations were carried out by shaking the freshly precipitated chelate with chloroform. An excess of dichloroxine was found to be necessary with both methods. Similar treatment of oxine systems showed them to have only a very slight chloroform solubility--on the order of 10^{-6} mole/liter. Although accurate figures have not been obtained, the dichloroxine chelates appear to be several hundred times as soluble.

B. Absorption Spectra

Regardless of the cation present, complexes of this type, at least in chloroform solution, exhibit absorption in the form of a very broad peak near 4000Å. It was of special interest to find, however, that certain peaks of a few of the rare earths undergo resolution, magnification in intensity, and displacement in their wave-lengths. Although nearly all of the rare earth ions have absorption peaks which are probably changed by complexing, only those whose affected peaks at wave lengths greater than approximately 5000Å may be considered. Others are ruled out by the intense 4000Å peak which characterizes all oxinate complexes regardless of the nature of the cation and which hides any other peaks that might be due to the cation alone.

With this limitation, only neodymium, holmium, erbium, thulium, and ytterbium appear suitable for treatment. Of these neodymium has been dealt with extensively; preliminary work has been undertaken with erbium. The 5745Å peak of the former has been shown to be enhanced to about ten times its height for the aqueous solution, to be divided into three peaks, and to be shifted to about 5820Å. The 5220Å peak of erbium is shifted to 5208Å, is about eight times higher, and is slightly altered in shape.

The neodymium peak (5820Å) obeys Beer's Law probably up to the maximum solubility of the compound. Exploratory examinations indicate that neodymium is not extracted into chloroform unless the pH of the system is equal to or above that required for precipitation of the hydroxide.

Further studies will be directed toward determining the effects of complexing on more rare earth spectra and toward establishing this method as an analytical procedure for micro-quantities of those elements whose peaks are altered measurably.

IV. Conclusions

Both the thermal instability of these materials when formed in the presence of water and the necessity for use of a large excess of reagent in extraction experiments can be taken as additional evidence for the partially ionic nature of rare earth inner complexes.

A fundamental interpretation of the spectral phenomena encountered awaits the collection and coordination of parallel data on several complex compounds of the rare earths.

A useful outgrowth has been the definition of a procedure suitable for the quantitative determination of micro-amounts of the lanthanons. The pH-dependence of extraction efficiency suggests a means of fractionation; however, since complex formation has been demonstrated to reduce the already slight basicity differences between these elements (11), there is little likelihood of sufficient selectivity by this method.

V. Appendix

Dichloroxine is commercially unavailable. Synthetic procedures have been reported (1,4,5), but attempts to repeat the most common of these, chlorination of oxine in cold, glacial acetic acid solution, have given at best only a fifty per cent yield. This reaction should be much more efficient since the similar bromination is used for a volumetric method.

VI. Bibliography

1. Berg, R., Z. anorg. Chem., 204, 208 (1932).
2. Berg, R., and Becker, E., Z. anal. Chem., 119, 1-4 (1940).
3. Downs, N., Thesis, Master of Science, University of Illinois, 1945.
4. Ghosh, T.N., Lasker, S.L., and Banerjee, S., J. Indian Chem. Soc., 21, 352-4 (1944).
5. Hebebrand, A., Ber., 21, 2980 (1888).
6. Kolthoff, I.M. and Sandell, E.G., "Quantitative Inorganic Analysis", Macmillan, New York, revised edition, 1946, p. 638.
7. Mannelli, B., Atti Congr. intern. chim., 2, 718-25 (1938).
8. Melent'ev, B.N. and Terekhovko, A.S., Trudy Kol'skoi Bazy Adad. Nauk USSR, 5, 71-6 (1940).
9. Pirtea, T.I., Z. anal. Chem., 107, 191-3 (1936).
10. Pirtea, T.I., Bul. Chim., Soc. Romane Chim., 39, 83-5 (1937-8).
11. Quill, L.L. and Stites, J.G., A Paper at the A.C.S. Meeting, San Francisco, Calif., March 1949.
12. Radoitchitch, M., Ann. chim., 13, 5-37 (1940).

ELECTROCHEMICAL STUDIES OF SOME COORDINATION COMPOUNDS OF SILVER

Alan L. McClelland

Thesis Report

May 16, 1950

Many compounds of divalent silver and a few compounds containing trivalent silver have been characterized in the solid state, but relatively little quantitative work on the stability of these compounds in solution has been done. It was therefore decided that measurement of the oxidation potentials of some of these compounds in solution would provide information of value in predicting uses for these compounds and would help to clarify relationships in the copper subgroup of the periodic classification.

Review of Compounds of Di- and Trivalent Silver (1,2)

The divalent oxide of silver, Ag_2O , has been shown by many investigators to be the true divalent oxide, and not a peroxide of monovalent silver as was formerly suggested. It is easily prepared in a high state of purity. It is relatively insoluble, dissolving only in solutions containing concentrations of hydrogen ion greater than one molar. The trivalent oxide has been reported, but it is unstable and has never been prepared in pure form. The basic salt usually given the formula $\text{Ag}_3\text{O}_2\text{NO}_3$ is a definite compound; its exact formula has not been determined.

Coordination compounds of divalent silver have been prepared containing the following donor molecules: pyridine, dipyridyl, tripyridyl, orthophenantroline, picolinic acid, and quinolinic acid. Trivalent silver has been reported to form coordination compounds with ethylenedibiguanide and with the periodate ion.

Noyes, et al., (3) found oxidation potentials for the silver (I)-silver (II) system of 1.929 and 2.000 volts vs. the hydrogen electrode at 25°C. in 4M nitric and perchloric acids respectively. They also studied the mechanism of the oxidation of silver nitrate in these solutions by ozone and of the oxidation of water by the divalent silver.

Measurement of Oxidation Potential of Pyridine Complex

Since oxidation of silver nitrate in the presence of pyridine with peroxydisulfate yields an insoluble silver (II) complex, electrolytic oxidation was tried as a method of preparing a solution of silver (II) pyridine complex ion. This method was not very successful since at low current densities a steady state was soon reached in which the divalent complex oxidized water as rapidly as it was formed, thereby giving only a very low concentration in solution. At higher current densities considerable oxidation of the pyridine occurred.

It was found possible to prepare a solution of the divalent complex by dissolving Ag_2O in 7M nitric acid and adding a small amount of this solution to a large excess of pyridine. The potential of a platinum electrode in this solution could be measured, and by substitution of the appropriate quantities in the Nernst equation the oxidation potential could be calculated. The following data summarize the measurements.

| | | | |
|--|----------|----------|-----------|
| Total Pyridine | 1.008 M | 0.506 M | 0.254 M |
| Total Silver | 0.026 M | 0.0202 M | 0.0216 M |
| Conc. Silver (II) (varied during each run) | | | |
| from | 0.0008 M | 0.0005 M | 0.00015 M |
| to | 0.0003 M | 0.0001 M | 0.00005 M |

| | | | |
|--|----------|----------|----------|
| Final pH | 5.88 | 5.78 | 5.22 |
| Effective Pyridine Concentration (Total Pyridine minus amount of pyridine present as pyridine- H^+ and amount coordinated to silver) | | | |
| | 0.776 M | 0.361 M | 0.103 M |
| E° (Calculated by the equation $E^{\circ} = E - 0.059 \log \frac{Ag(II)}{Ag(I)}$) | | | |
| | 1.341 v. | 1.365 v. | 1.422 v. |

Calculated Values for Silver (II) Pyridine Complex ion.
 $E^{\circ} = 1.33$ v. vs. hydrogen electrode at 25°C.
Average number pyridine molecules per divalent silver ion, 3.5
Dissociation constant, 10^{-15}

The concentration of the divalent silver in the solution was determined by adding a pipetted sample of the solution to excess standard sodium arsenite solution and back-titrating the arsenite with ceric sulfate solution. Since the concentrations of divalent silver were so low, the ordinary methods of detecting the end point for this titration were not applicable and an amperometric method was developed. Since this method had never been used for this titration, it was necessary to show that it was accurate. It was found that this method was accurate to at least one percent for 0.001 M arsenite and ceric sulfate solutions, rapid, and convenient.

Since the divalent silver concentration decreased steadily on standing, presumably due to reduction by water, the kinetics of the reaction were studied in an attempt to deduce the mechanism. The reaction was found to be a mixed first- and second-order reaction with respect to divalent silver. The interpretation of these results is not yet complete.

Measurement of Oxidation Potential of Dipyridyl Complex

It was found that the dipyridyl complex of divalent silver is stable enough to be formed by the action of ceric nitrate in 1M nitric acid on a solution of silver nitrate and dipyridyl in 1M nitric acid. Therefore the easiest way to study the oxidation potential of the system was to titrate monovalent silver with standardized ceric nitrate solution in the presence of dipyridyl, following the titration potentiometrically. The following results were obtained:

| | | | |
|-----------------|----------|----------|----------|
| Total dipyridyl | 0.065 M | 0.126 M | 0.834 M |
| E° | 1.470 v. | 1.438 v. | 1.362 v. |

Preliminary calculations indicate two molecules of dipyridyl coordinated to each divalent silver ion in solution. The E° value based on these calculations is 1.33 volts vs. the hydrogen electrode at 25° C.

Work is in progress at present on the measurement of the potential of the orthophenanthroline complex. Preliminary results indicate that it is more stable than the dipyridyl complex.

- (1) Bailar, J.C., Jr.; J. Chem. Education 21, 523-5 (1944).
- (2) Kleinberg, J.; Unfamiliar Oxidation States and Their Stabilization, U. of Kansas Press, Lawrence, 1950, 51-73.
- (3) Noyes, A. A., et al; J. Am. Chem. Soc. 57, 1221-42 (1935), 59, 1316-37 (1937).

R. Keith Osterheld

Thesis Report

May 23, 1950

High temperature reactions constitute an important phase of the chemistry of phosphates. The phosphates resemble the molybdates, chromates, and vanadates with respect to the formation of isopolyacids. However, unlike these particular anions, it is necessary to make use of high temperature acid systems to form the condensed phosphates. In aqueous solution, only depolymerization or so-called "reversion" reactions take place, the condensed phosphates ultimately being converted to orthophosphate. The use of high temperature bases, such as alkali metal halides, to effect these depolymerizations offers a possible approach to the preparation of a halophosphate.

A. Thermal Analysis Equipment

Considerable use was made of the technique of differential thermal analysis in these investigations. A small muffle type electric furnace was used for heating the samples. Sample temperatures were recorded continuously by means of an automatic recorder. The differential in temperature between the sample and a similar amount of ignited aluminum oxide was recorded simultaneously on a second recorder. The temperature sensing units for both these purposes were Pt-90Pt10Rh thermocouples. The thermocouple and recorder combination used to determine the sample temperature was calibrated periodically.

For those cases in which heating curve data were required, the heating rate was controlled to eight to ten degrees per minute. This was accomplished through the use of a controller to maintain a constant differential (about 10°) between the furnace muffle and the aluminum oxide sample.

B. The System Sodium Fluoride-Sodium Metaphosphate

The system potassium fluoride-potassium metaphosphate had been studied by Amadori (1). The data for the system reveal the existence of two compounds: the monofluophosphate, $\text{KF} \cdot \text{KPO}_3$ or $\text{K}_2\text{PO}_3\text{F}$, which possesses a congruent melting point; and $2\text{KF} \cdot \text{KPO}_3$, which melts incongruently. Sodium monofluophosphate has been shown to form when sodium fluoride and sodium metaphosphate are heated together (4). The thermal stability characteristics of this material were not determined. For this reason, and, also, in order to contrast the weaker base, sodium fluoride, with the potassium compound, the system sodium fluoride-sodium metaphosphate was investigated from 0 to 60% NaPO_3 . Melts richer in sodium metaphosphate would not crystallize reproducibly upon cooling; the melt at 80% NaPO_3 cooled to a glass.

The phase diagram constructed from cooling curve data shows that two compounds form in this system. The monofluophosphate, $\text{Na}_2\text{PO}_3\text{F}$ melts incongruently at 566° and undergoes two solid-phase transitions at 406° and 357° . The magnitudes of the cooling curve breaks corresponding to these temperatures exhibit maxima at the 1:1 mol ratios. A second compound, $2\text{NaF} \cdot \text{NaPO}_3$, melts congruently at 655° . Cooling curves near the 2:1 composition show a strong break at 566° , corresponding to the formation of monofluophosphate. Consequently, the 2:1 compound must be considered unstable with respect to sodium fluoride and monofluophosphate below 566° . Although analogous compounds form in the sodium and potassium systems, it is interesting that the thermal stability characteristics are reversed. Sodium fluoride and the compound $2\text{NaF} \cdot \text{NaPO}_3$ form an eutectic mixture at 15.8% NaPO_3 (nominal) and melting at 615° . The

eutectic composition corresponds to a mixture of 23.1% ($2\text{NaF} \cdot \text{NaPO}_3$) and 76.9% NaF . A second eutectic, formed between $\text{Na}_2\text{PO}_3\text{F}$ and NaPO_3 , exists in the area richer than 60% in sodium metaphosphate. Its position could not be determined by the use of cooling curves since the high metaphosphate content inhibited crystallization.

C. The Systems Sodium Chloride-Sodium Metaphosphate and Potassium Chloride-Potassium Metaphosphate

Although the chloride ion would be expected to be a weaker base than fluoride, there was a possibility that alkali metal chlorides might serve to depolymerize the corresponding metaphosphates and produce chlorophosphates.

The sodium chloride-metaphosphate system was investigated sufficiently to demonstrate that no chlorophosphate is obtained. The corresponding potassium compounds had been reported previously to form only a eutectic (2). This earlier work was verified.

The samples in both chloride-metaphosphate systems were found to undergo extensive decomposition (as evidence by weight losses) while in the molten state. Considerable attack of the platinum crucibles was observed. Less decomposition was noted in the case of fluoride-metaphosphate melts, with no noticeable attack of the platinum.

D. The System Potassium Pyrophosphate-Potassium Metaphosphate

The binary systems sodium pyrophosphate-sodium metaphosphate and potassium pyrophosphate-potassium metaphosphate were first investigated by Parravano and Calcagni (5). No evidence of compound formation was reported. Partridge, Hicks, and Smith (6) reinvestigated the sodium pyrophosphate-metaphosphate system and demonstrated that sodium triphosphate forms. Since the formation of sodium triphosphate had been overlooked in the earlier work, it seemed likely that a similar error may have been made in the study of the corresponding potassium system. The tendency of the larger potassium ion to stabilize discrete polyanionic units (3) made this even more probable. It was also hoped that this stabilizing factor might make possible the formation of a potassium tetrphosphate.

Samples for this investigation were prepared by thoroughly mixing and grinding together appropriate proportions of potassium dihydrogen and monohydrogen orthophosphate. Each mixture was heated for two hours at 575° , removed, ground thoroughly, and then replaced for another two hour period at 575° .

The data for constructing this system were obtained from heating curves since it seemed likely that the transitions would not take place rapidly enough to give distinct arrests on cooling. The diagram constructed from these data showed potassium triphosphate to form as a compound melting incongruently at 650° . This compound forms an eutectic mixture with potassium metaphosphate at about 74.3% KPO_3 (nominal). The eutectic melts at 620° and corresponds in composition to an actual mixture containing 34.6% $\text{K}_5\text{P}_3\text{O}_{10}$ -65.4% KPO_3 .

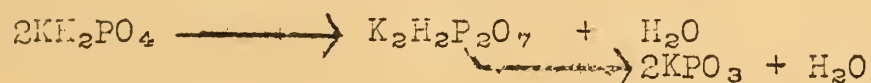
Samples corresponding to compositions from 50 to 85% KPO_3 were analyzed for pyrophosphate, triphosphate, and metaphosphate before being subjected to thermal analysis to determine whether any evidence for the formation of a potassium tetrphosphate could be found. If it formed, this compound would occur at 66.7% KPO_3 in this system.

The results of the analyses demonstrate clearly that these samples contain only triphosphate and metaphosphate; tetraphosphate does not form (in samples prepared at 575°).

E. Mechanism of the Potassium Dihydrogen-Monohydrogen Orthophosphate Reaction

The use of this reaction to prepare the samples for investigation of the potassium pyrophosphate-metaphosphate system led to consideration of the mechanisms 1) by which the potassium hydrogen orthophosphates react to form the triphosphate and 2) by which the individual reactants undergo dehydration.

Thermal analysis of potassium dihydrogen orthophosphate showed that the rate of dehydration becomes appreciable at 208°. A strong endothermic process takes place at 258°, during which water is lost rapidly and the material froths. Since it is possible to prepare disodium dihydrogen pyrophosphate by partial dehydration of sodium dihydrogen orthophosphate at 210°, it was anticipated that potassium dihydrogen orthophosphate might also dehydrate in the steps:



However, heating of samples at temperatures between 208° and 258° showed that water was lost smoothly until complete dehydration to metaphosphate had occurred. Analyses of samples taken at various stages during the dehydration showed that metaphosphate formed early in the reaction. At no time was there present any appreciable amount of pyrophosphate or of any other intermediate.

This indicated that dipotassium dihydrogen pyrophosphate was too unstable thermally to be isolated in such a reaction. Thermal analysis of the compound obtained in another way proved that its dehydration commenced below 200° and became rapid at 232°.

The heating curve for potassium monohydrogen orthophosphate demonstrated that the conversion into pyrophosphate proceeds in two steps: the first from 282° to 332°, and the second between 400° and 462°. Samples of anhydrous potassium monohydrogen orthophosphate were found to lose 55% of their constitutional water at 325° and a total of 105% upon being heated to 460°. With the exception of several minor lines, all the lines in the x-ray diffraction pattern of the intermediate material could be ascribed to K_2HPO_4 , the starting material, and to $\text{K}_4\text{P}_2\text{O}_7$, the ultimate product. Analyses of the "half-dehydrated" material showed it to contain 51.3% of the P_2O_5 content as pyrophosphate.

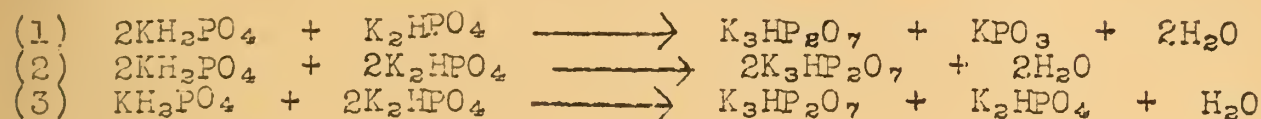
Thermal analyses of samples containing 2:1, 2:2, 3/2:2, and 1:2 mole ratios of potassium dihydrogen to monohydrogen orthophosphate indicated that in each case a reaction started around 180-200° and became steady in the region between 230° and 250°. Comparison with the heating curves for the pure reactants made it clear that this reaction is not due to either component acting as an individual.

A temperature of 245° was chosen as one which would be likely to bring this initial reaction to completion. Samples containing 2:1, 2:2, and 1:2 mole ratios of potassium dihydrogen to monohydrogen orthophosphate were heated to constant weight at 245°. A comparison of weight loss data and analyses of the products with the results predicted by

the various possible reactions indicates that the major reaction at this temperature is:



Strong evidence for this is the fact the the x-ray diffraction pattern of the 2:2 mole ratio product does not contain the strong lines of any of the common potassium phosphates. For the three mole ratios investigated here, the complete reactions at 245° are:

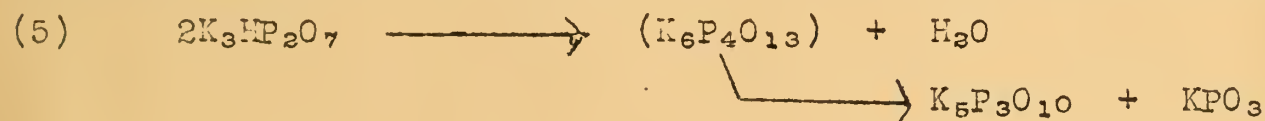


The mixtures in equations (2) and (3) are of particular interest, (2) because it involves a new compound and (3) because upon heating to a sufficiently high temperature it forms potassium triphosphate. The constant weight products at 245° of equations (2) and (3) were subjected to thermal analysis to determine their behavior at higher temperatures.

The major reaction in the $\text{K}_3\text{HP}_2\text{O}_7$ - K_2HPO_4 mixture produced by equation (3) was found to have been completed by about 320°. Samples heated to constant weight at 325° were found to have been essentially completely converted to triphosphate. This reaction may be represented by the equation:



Thermal analysis shows that further reaction of $\text{K}_3\text{HP}_2\text{O}_7$, obtained as a product of the process represented by equation (2), takes place at a somewhat higher temperature, being completed at about 350°. Heating to constant weight at 325° will complete the reaction, however. The product was found by analysis to contain 24.0% and 75.6% of its P_2O_5 content as metaphosphate and triphosphate, respectively. It may be postulated that an unstable tetraphosphate intermediate forms and subsequently disproportionates in accordance with the following equation:

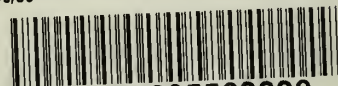


F. Bibliography

1. Amadori, M., Atti reale acad. Lincei 21 II, 183 (1912).
2. Amadori, M., *ibid*, 21 II, 638 (1912).
3. Flood, H., and Forland, T., Acta Chem. Scand. 1, 592 (1947).
4. Hill, O. F., Ph.D. Thesis, University of Illinois, 1948.
5. Parravano, N., and Calcagni, G. Z. anorg. Chem. 65, 1 (1910)
6. Partridge, E. P., Hicks, V., and Smith, G. W., J. Am. Chem. Soc. 63, 454 (1941).



UNIVERSITY OF ILLINOIS-URBANA
546IL6I C001
INORGANIC SEMINAR ABSTRACTS URBANA
1949/50



3 0112 025502920